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SOME DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE.[1]

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The action of methyl alcohol on tetrabromorthobenzo quinone was studied by Porter and one of us[2] and was found to be comparatively simple, consisting, if the reaction was carried on at ordinary temperatures, in the formation of two compounds:

a. $(C_6Br_4O_2)_4CH_3OH$.[3]

b. The α-body, octobromorthoquino-1-methoxy-1′-hydroxy-1-monoxide,[4] $C_6Br_4OOCH_3OHOOC_6Br_4$.

By the action of various reagents *b* was changed into *c*, the isomeric β-compound, octobromorthoquino-1-methoxy-

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy by Robert D. MacLaurin.

[2] THIS JOURNAL, **31**, 95 (1904).

[3] Jackson and H. A. Carlton: THIS JOURNAL, **34**, 425 (1904).

[4] *Ibid.*, **37**, 87 (1907).

1′-hydroxy-1,2,2-trioxide, $C_6Br_4OCH_3O_3HOC_6Br_4$, but this substance has never been obtained by the action of cold methyl alcohol on tetrabromorthoquinone.

The action of cold methyl alcohol on tetrachlororthobenzoquinone, $C_6Cl_4O_2$, has been studied by us for nearly three years, and in this paper we give the results of this work, which has led to the isolation of six products.

1. The *β*-compound, octochlororthoquino-1-methoxy-1′-hydroxy-1,2,2-trioxide, $C_6Cl_4OCH_3O_3HOC_6Cl_4$, melting at 157°, without decomposition.

2. 3,5,6-Trichlor-4-methoxyorthobenzoquinonemonomethylhemiacetal, $C_6Cl_3OCH_3O(OCH_3OH)$, melting at 138°–140° without apparent decomposition.

3. 3,5,6-Trichlor-2-hydroxyparaquinone, $C_6Cl_3OHO_2$, orange plates melting at 198° to a pale brown liquid.

4. Chloranilic acid, $C_6Cl_2(OH)_2O_2$.

5. Hexachlororthoquinomonomethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O(OCH_3OH)$, yellow needles melting at 198°, with reddening.

6. Hexachlororthoquinodimethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2(OCH_3OH)(OCH_3OH)$, white plates melting at 218° to a fawn-colored liquid.

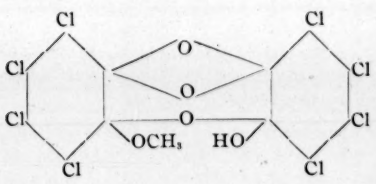
These observations add another case to the list of those, in which chlorine and bromine derivatives act differently, the two series having no members in common, for, although 1 and *c* belong to the same class, the correspondence is rather apparent than real, because the *β*-chlor compound (1) was made by the action of cold methyl alcohol on the quinone, whereas the *β*-brom compound (*c*) has never been obtained in this way. In our first experiment, to be sure, we obtained a substance, which seemed to be the *α*-compound $(C_6Cl_4O_2)_2CH_3OH$ (corresponding to *b*) to judge from a single chlorine determination and its properties, but, as we have never succeeded in making this body again, although we have tried a great number of experiments under the most varied conditions we could devise, we do not feel justified in announcing its existence.

The principal cause of the difference between these two series consists in the fact that with the bromine compounds the action

is confined to the atoms of oxygen, whereas in the chlorine compounds (except 1), the halogen also takes part in the reaction. This easier replacement of the chlorine is the more strange, because in an earlier paper[1] we have shown that in the substituted dianilinoparaquinoneanils the reverse is true, bromine being replaced decidedly more easily than chlorine. Further experiments will be necessary to determine, whether this difference in behavior is caused by the presence of the anilino groups, or by the fact that these bodies are derivatives of para instead of orthoquinone.

In the following accounts of these six compounds we give our reasons for the constitution assigned to each, while the details of our work will be found in the Experimental Part.

1. *The β-compound,* $C_6Cl_4OCH_3O_3HOC_6Cl_4$, *Octochlororthoquino-1-methoxy-1'-hydroxy-1,2,2-trioxide.*—This substance was formed, when tetrachlororthoquinone was allowed to stand in the cold with methyl alcohol in the proportion of 1–5 cc. to each gram. It crystallizes in rhombic plates, which melt without change of color at 157°. These properties, with the analytical results, are sufficient to characterize it as the β-compound. Its structure, therefore, is represented by the following formula[2]



2. *3,5,6-Trichlor-4-methoxyorthobenzoquinone monomethylhemiacetal,* $C_6Cl_3OCH_3O(OCH_3OH)$. This substance was the principal product, when 8–12 cc. of cold methyl alcohol were used for each gram of the tetrachlororthoquinone. It forms

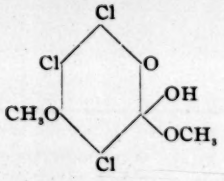
[1] This Journal, **37**, 10 (1907).
[2] *Ibid.*, **37**, 87 (1907).

white, thick rhombic plates, which melt at 138°–140° to a colorless liquid, changing to red after standing in the hot bath for 5 minutes. Its constitution was determined by the following observations:—Molecular weight determinations by the boiling point process showed it contained only one benzene ring. Acetic anhydride gives a monacet derivative,

$$C_6Cl_3OCH_3O(OCH_3OC_2H_3O),$$

melting at 149°–150°, indicating the presence of only one hydroxyl group; this acet compound forms a hydrazone (melting point 235°) with phenylhydrazine, and the substance, therefore, contains a keto group. Strong hydrochloric acid converts it into the 3,5,6-trichlor-2-oxyparabenzoquinone, $C_6Cl_3OHO_2$, and this reaction undoubtedly consists in the conversion of the body first into 3,5,6-trichlor-4-oxyorthoquinone, which then, by the usual shifting of the hydrogen, is changed into the paraquinone.

The hemiacetal itself is not derived from a paraquinone, since it is formed from the tetrachlororthoquinone. The formation of chloranilic acid from the substance by the action of sodic hydrate proves that the methoxyl is not at 3 or 6, but must stand at 4 or 5. The white color of the compound is in harmony with what is known of quinone hemiacetals, but its stability is decidedly greater than that of the hemiacetals derived from paraquinones. The substance is, therefore, the monomethylhemiacetal of the 3,5,6-trichlor-4-methoxyorthoquinone, melting at 93°–94°, discovered by Zincke and Schaum,[1] and is represented by the following formula,



1 Ber. d. chem. Ges., 27, 555 (1894).

in which the position of the hemiacetal group with reference to the methoxyl has not been determined.

So far as we can find but one other hemiacetal of an orthoquinone has been prepared. This was made by Zincke and Schaum,[1] and has the formula, $C_6Cl_3OCH_3(OCH_3)_2(OHOCH_3)$. The following hemiacetals of diketo compounds are, however, closely related to orthoquinone hemiacetals;

$C_{10}H_4Cl_4O(OHOCH_3)^1/_2H_2O^2$ and $C_{10}H_6OCH_3O(OHOCH_3)NO_2$[3].

On one occasion a yellow product melting at 210° was formed by shaking the monohemiacetal (2) with methyl alcohol and hydrochloric acid. A single determination of chlorine gave a result corresponding to a dichlordimethoxyquinone, but, as we did not succeed in making it again, its existence cannot be considered established.

3. 3,5,6-Trichlor-2-oxyparaquinone, $C_6Cl_3OHO_2$.—This substance was obtained in hexagonal orange plates from the mother liquors of the *β*-compound (1) made by the action of cold methyl alcohol on tetrachlororthoquinone in the proportion of 2 cc. to each gram. It was more conveniently prepared by the action of hydrochloric acid on the monomethylhemiacetal (2).

At first we supposed that this compound was the 4-oxyorthoquinone, but, as its melting point, 198°, was not far from 194°, that of the 3,5,6-trichlor-2-oxyparaquinone of Zincke and Schaum,[4] it seemed more probable that the 4-oxyorthoquinone, which must have been the original product, had become converted into this oxyparaquinone. To test this point the acet compound, $C_6Cl_3OC_2H_3OO_2$, melting at 127°, was made and reduced by sulphurous anhydride to the dihydroxy compound, $C_6Cl_3OC_2H_3O(OH)_2$, which was tested for orthohydroxyls with ferric chloride, plumbic acetate, and picric acid, and as all of these tests gave negative results, there can be no doubt that our substance is not an orthoquinone. To establish more securely the identity of our product with that of Zincke and Schaum it was reduced with sulphurous dioxide to the oxyhydroquinone,

[1] Ber. d. chem. Ges., **27**, 551 (1894)
[2] Zincke and Arnst: Ann. Chem. (Liebig), **267**, 332 (1892).
[3] Zincke and Neumann: *Ibid.*, **278**, 173 (1893).
[4] Ber. d. chem. Ges., **27**, 556 (1894).

$C_6Cl_3(OH)_3$, and this melted at 162° which is 2° higher than the melting-point given by them; but the triacetyl compound, $C_6Cl_3(OC_2H_3O)_3$, made from it showed the melting point 171°, the same as that observed by them. There can be no doubt, therefore, that our compound is identical with that of Zincke and Schaum in spite of these slight differences in melting points. That it is a 2-hydroxy compound is proved by its easy conversion into chloranilic acid.

4. *Chloranilic Acid*, $C_6Cl_2(OH)_2O_2$.—This body was obtained from the mother liquors, which also yielded the oxyparaquinone (3). That it was chloranilic acid and not an isomer was proved by a careful comparison of our product with chloranilic acid from chloranil, the details of which are given in an earlier paper.[1]

The appearance of these two hydroxyl compounds as products of the action of methyl alcohol is striking. The saponification of the methoxyl bodies formed at first may have been due to the hydrochloric acid also produced by the action of methyl alcohol on tetrachlororthoquinone, or, as they were obtained from mother liquors which had been exposed to the air for a long time, they may have owed their formation to atmospheric moisture, or even, perhaps, the ammonia in the air of the laboratory may have taken part in the reaction.

5. *Hexachlororthoquinomonomethylhemiacetalpyrocatechin Ether*, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—This product of the action of methyl alcohol on tetrachlororthoquinone crystallizes in yellow needles, melting at 198°. As the orange oxyparaquinone, $C_6Cl_3OHO_2$ (3) also melts at 198°, we give a comparison in tabular form of some of the more striking properties of these substances to show that they are different.

Trichloroxyparaquinone	*Hexachlormonohemiacetal*
Mol. wt. 227.	Mol. wt. 457.
Orange leaflets	Yellow needles
Purple solution with water	No action with water
Sulphuric acid decomposes it	Sulphuric acid gives red, $C_6Cl_4O_2.C_6Cl_2O_2$.
Acet compound brassy plates, melting at 127°.	Acet compound pale yellow, cauliflower-like masses, melting at 215°.

[1] This Journal, 37, 97 (1907).

This table would not have been needed, if our analytical results had been decisive. Unfortunately this is not the case, for, although one combustion agreed with the formula given above, a second gave different results, and the work was done so late that there was not time to prepare sufficient substance for a new determination. The hemiacetal formula, however, agrees so well with all the observed facts, that there is little doubt of its correctness, and it can be accepted, until the final proof is given by new combustions and experiments which will be made when the work is continued in this laboratory.

The arguments in favor of the formula assigned to this substance follow. That it is a derivative of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, is shown by its quantitative conversion into this substance, when treated with strong sulphuric acid, and by its formation from this ether by the action of methyl alcohol. This last reaction also indicates that it is probably a hemiacetal; and this indication is raised nearly to a certainty by its formation from the trichlormethoxymonomethylhemiacetal, (2, the constitution of which has been established) and tetrachlororthoquinone in methyl alcohol solution, as shown by the following reaction:

$$C_6Cl_4(OH)_2 + C_6Cl_3OCH_3O(OCH_3OH) = C_6Cl_4O_2C_6Cl_2O(OCH_3OH) + HCl + CH_3OH,$$

in which the tetrachlorpyrocatechin may have been produced by the action of the methyl alcohol on the orthoquinone, or more probably after the reaction has started, by the hydrochloric acid formed. The removal of methyl alcohol in such a reaction is an unusual phenomenon, but not without analogy, as Grindley and one of us[1] found that the phenoxy group in paraquinone derivatives was easily replaced by the methoxy, or malonic ester radical.

The light color of the substance is characteristic of the hemiacetals, and we saw some indications of the formation of a sodium salt, which would be expected from such a compound, although longer treatment with sodic hydrate converted it into

[1] This Journal, 17, 597, 600 (1895).

the chloranilate—a reaction which would be expected from a derivative of the hexachlororthoquinopyrocatechin ether.

On the other hand, hydrochloric acid does not decompose it so easily as we should expect from the properties of the para-hemiacetals, but all our experience shows that orthohemiacetals are much more stable than those belonging to the para series.

In the hope of throwing light on the structure of this compound we tried the action of acetic anhydride on it, but the results were decidedly puzzling, for under the conditions used by us the substance was first converted, in part at least, into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, and then the further action of the acetic anhydride yielded a white product,[1] giving analytical results corresponding to $C_{12}Cl_6O_4(C_2H_3O)_2$, which should have been the hexachlororthodiacetoxypyrocatechin ether, but melted at 215°, whereas the true diacetoxy ether, $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$ (prepared from the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$) melted at 282°. Beside this difference of 67° in the melting point there were differences in color, crystalline habit, and solubility, the most striking being that the compound melting at 215° dissolved in sodic hydrate, but the one melting at 282° did not. We are of the opinion, therefore, that the two products are different compounds rather than one compound in different degrees of purity. At first we supposed that the case was similar to that observed by Russe and one of us,[2] when tetrabromorthobenzoquinone gave with benzoyl chloride a dibenzoate melting at 172°–174°, whereas the compound with the same composition made from tetrabrompyrocatechin melted at 197°, but this proved to be a mistaken supposition, for on treating the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, with acetic anhydride we obtained a diacetate melting at 280°–282°, identical with that made from the dihydroxy ether. More work will be necessary before we are able to give any explanation of these strange observations.

6. Hexachlororthoquinodimethylhemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$.—The last of the principal products of the methyl alcohol reaction crystallized in white

[1] Later experiments have shown that this substance is $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$. —C. L. J.

[2] This Journal, **35**, 169 (1906).

plates melting to a pale fawn-colored liquid at 218°. A determination of the molecular weight of this substance indicated that its formula was $(C_6Cl_3OCH_3O_2)_3$, but the following considerations have led us to believe that this determination gave a false result,[1] and that its real formula is $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, which agrees quite as well with the analyses. The substance is converted easily into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, this change taking place at a temperature somewhat above its melting point, or by heating it gently with strong sulphuric acid, while hydrochloric acid or reduction yields the dihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, formed by the subsequent reduction of the quino ether, which must have been the original product. The amount of the red ether formed by sulphuric acid agreed well with the quantities calculated from $2(C_6Cl_3OCH_3O_2)_3$ to $3\ C_6Cl_4O_2C_6Cl_2O_2$, or from $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$ to $C_6Cl_4O_2C_6Cl_2O_2$, but, whereas in the last case the formation of the red ether is a most natural reaction, we have not been able to devise any arrangement of the atoms in the first formula, $(C_6Cl_3OCH_3O_2)_3$, which would account for its quantitative formation, since this reaction shows that the group C_6Cl_4 must be present in our substance, leaving Cl_5 to be apportioned between 2 benzene rings, and no arrangement of this can furnish at once the C_6Cl_4 and the C_6Cl_2 needed to form the third molecule of the ether for the quantitative conversion without more violent transformations than could be expected under the conditions of this reaction.

The formation of this substance (*6*) from the preceding by the action of methyl alcohol and hydrochloric acid indicates that it is the complete hemiacetal, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, and this is confirmed by its white color, and the apparent formation of a very unstable salt with potassic hydrate, which soon passed into potassic chloranilate. The action of acetic anhydride, which should have given a diacet derivative, seemed to give the unaltered substance in a somewhat impure condition; the resistance to this action may have been due to steric conditions. We hope that

[1] The need of this revision was discovered too late to repeat the work.

further work in this laboratory will soon furnish an experimental proof of the correctness of the formula assigned to it.

The most astonishing observation made by us in the course of this work was the conversion of trichloroxyparaquinone into derivatives of tetrachlororthoquinone. On three occasions in making the β-compound, $C_6Cl_4OCH_3O_3HOC_6Cl_4$, by the action of methyl alcohol on tetrachlororthoquinone its appearance was preceded by the formation of orange crystals, that seemed to be the oxyparaquinone, $C_6Cl_3OHO_2$, which, after standing 24 hours longer, were replaced by the white crystals of the β-compound. As these experiments did not necessarily prove that the β-compound was formed from the oxyparaquinone, we next allowed a pure specimen of the trichloroxyparaquinone, $C_6Cl_3OHO_2$, melting at 198°, to stand with methyl alcohol and a little hydrochloric acid. At the end of six months a white product had separated, which was proved by its melting point, 218°, and a chlorine determination to be the hexachlororthomethylhemiacetalpyrocatechin ether,[1] $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, so that we had here the conversion of a paraquinone into a derivative of an orthoquinone, for the close relation of this hemiacetal to the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, leaves no doubt as to its being a derivative of orthoquinone. Although we feel certain of the accuracy of our observation in this case, we cannot consider this reaction established by a single experiment, since it is out of harmony with all previous experience, requiring, as it does, not only the conversion of a para into an orthoquinone, but also the replacement of a hydroxyl attached to the benzene ring by chlorine under the influence of hydrochloric acid in the cold. Our account of this work, therefore, must be taken as a preliminary announcement, until it has been submitted to the test of further experiment.

We have also studied the behavior of tetrachlororthoquinone with other substances, but lack of time has prevented us from investigating these products so thoroughly as those from methyl alcohol. The action of other alcohols on tetrabromorthoquinone

[1] This substance was obtained instead of the β-compound, because we used 7.5 cc. of methyl alcohol instead of 1.5 cc.

was, in general, simple like that of methyl alcohol, compounds of the α-series being obtained as the direct products,[1] but with tetrachlororthoquinone as a rule, different and more complex results were obtained.

Ethyl alcohol gave in the cold with tetrachlororthoquinone four compounds: the 3,5,6 trichlor-2-oxyparaquinone, $C_6Cl_3OHO_2$, chloranilic acid, $C_6Cl_2(OH)_2O_2$; a product crystallizing in white plates melting without decomposition at 115° to which we can assign no formula; and, as the principal product, a yellow compound crystallizing in rhombic plates and melting at 210° to a red liquid.

Analyses and a molecular weight determination of this last substance agree with the formula, $C_{28}Cl_{12}O_{10}H_{12}$, and this is confirmed by a chlorine determination and molecular weight of its diacet derivative. It would seem, therefore, to be made up up of 2 molecules of the orthoquinopyrocatechin ether combined with 2 of ethyl alcohol, $(C_6Cl_4O_2C_6Cl_2O_2)_2(C_2H_5OH)_2$. This view of its constitution is in harmony with the fact that it is converted into this ether with great ease, by heat, or nearly quantitatively by the action of strong sulphuric acid, and that it was prepared from it by the action of ethyl alcohol. We have not data enough to attempt an explanation of its structure, but it certainly shows some analogy to the α-compounds derived from tetrabromorthoquinone. Two other compounds melting at 210° have been encountered in the course of our work, but as one is a derivative of methyl alcohol, and the other of propyl alcohol they must be different from this ethyl compound.

Of the other alcohols of the fat series, tried with tetrachlororthoquinone, normal propyl alcohol and isoamyl alcohol gave the 3,5,6-trichlor-2-oxyparaquinone, melting at 198°, and chloranilic acid; isopropyl alcohol only chloranilic acid; tertiary butyl alcohol, on the other hand, formed a product, which we think is the β-addition compound, $C_6Cl_4OC_4H_9O_3HOC_6Cl_4$, octochlororthoquino-1-tertiarybutyloxy-1′-hydroxy-1,2,2-trioxide, because it crystallized in the rhombic plates characteristic of

[1] Jackson and Porter: THIS JOURNAL, 31, 100 (1904). Jackson and Carlton: *Ibid.*, 34, 429 (1905).

that series, but we cannot feel certain of this, since the other β-compounds melt without decomposition, while this substance forms a dark liquid on melting, not, however, the red ether characteristic of the α-bodies. Further, it is soluble in sodic hydrate, whereas the other β-compounds are not.

When benzyl alcohol acted on tetrachlororthoquinone, there was formed very quickly a yellow substance melting to a red liquid at 215°, and the same product was obtained by heating tetrachlororthoquinone with undried toluene.[1] The analyses showed it had a composition approaching $C_2Cl_6O_4H_2$, although it might contain more hydrogen, but at present we are unable to propose any structural formula for this body in spite of the fact that it shows many well-marked reactions.

When tetrachlororthoquinone was allowed to stand in the cold with undried toluene four products were obtained: *1.* Tetrachlororthoquinone with toluene of crystallization, $C_6Cl_4O_2C_7H_8$, which lost the toluene completely in *vacuo*. *2.* The α-water compound, octochlororthoquino-1-1′-dihydroxy-1-oxide, $C_6Cl_4OOHOHOOC_6Cl_4$, was formed, when the first product was allowed to stand longer with the toluene. It was characterized as an α-compound by the facts that it crystallized in needles and turned red on melting at 172°. *3.* A small quantity of an unidentified brown compound melting at 182°–183° was obtained. *4.* By still longer standing with the toluene a yellow compound melting and turning red at 290° was formed, which gave analytical results corresponding to the formula $C_{24}HCl_{13}O_8$. It is, therefore, probably made up of one molecule of the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, and one of the heptachlororthoquinopyrocatechin hemiether, $C_6Cl_4OHOC_6Cl_5O_2$. This theory is in harmony with the easy conversion of the substance into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, by heat, nearly quantitatively by boiling with water, or partially even on exposure to the air, since the heptachlorhemiether itself must pass into the red ether with the greatest ease. More experimental work is needed to determine how the two ethers are united in the substance melting at 290°.

[1] Under the same conditions tetrabromorthoquinone gave heptabromorthoquinopyrocatechin hemiether, $C_6Br_4OHOC_6Br_5O_2$. THIS JOURNAL, **35**, 165 (1905).

The behavior of the tetrachlororthoquinone with toluene is like that of the tetrabrom compound so far as the first 2 products are concerned, but no substances corresponding to *3* and *4* were observed in the bromine series. The formation of the α-water compound, $(C_6Cl_4O_2)_2H_2O$, from ordinary toluene and the orthoquinone turned our attention again to the strangeness of this reaction, for, as in our previous work with tetrabromorthoquinone, it was hard to believe that the apparently dry toluene contained enough moisture for the reaction, especially since some earlier experiments gave the water compound even with toluene supposed to be dry. We have, therefore, repeated the experiment with scrupulously dried materials, and found, as was to be expected, that the only product was the tetrachlororthoquinone with toluene of crystallization. It follows, therefore, that the tetrachlor- or bromorthoquinone has a remarkable attraction for water removing it from toluene or similar solvents, even when present in minute amount.

When tetrachlororthoquinone was allowed to stand for a long time in the cold with glacial acetic acid, the α-compound octochlororthoquino-1-acetoxy-1′-hydroxy-1-oxide, $C_6Cl_4OOC_2H_3OOHOOC_6Cl_4$, was formed, crystallizing in white needles and melting to a red liquid at 250°–252°. This is the only case observed in which the behavior of the tetrachlororthoquinone is simpler than that of the brom compound, since the latter with acetic acid forms at least four different products,[1] the structure of most of which still remains to be determined.

Warming the tetrachlororthoquinone with water for a few minutes converted it into the ether, $C_6Cl_4O_2C_6Cl_2O_2$.

Some derivatives of the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2.C_6Cl_2O_2$, were also prepared. With methyl alcohol it gave the hexachlororthoquinomonohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OHOCH_3)$(*5*), melting at 198°, discussed earlier in this paper. If a little water was added to the methyl alcohol, in addition to this product the complete acetal, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$(*6*), melting at 218°, and chloranilic acid were identified.

[1] Jackson and Koch: THIS JOURNAL, **26**, 42 (1901). Jackson and Porter: *Ibid.*, **31**, 115 (1904). Jackson and Russe: *Ibid.*, **35**, 178 (1906).

Ethyl alcohol with the ether, $C_6Cl_4O_2C_6Cl_2O_2$, gave chloranilic acid and the product melting at 210° formed by ethyl alcohol and the tetrachlororthoquinone. Normal propyl alcohol also gave a product melting at 210°, which must, however, have been different from that prepared with ethyl alcohol. Phenylhydrazine reduced the orthoquino ether to the hexachlordihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$. Shaffer and one of us[1] observed a similar reduction of the hexabrom ether with phenylhydrazine, while with methyl alcohol it gave very slowly the complete acetal, $C_6Br_4O_2C_6Br_2(OCH_3OH)_2$, melting at 220°–221°.

EXPERIMENTAL.

Action of Methyl Alcohol on Tetrachlororthobenzoquinone.—The tetrachlororthoquinone used by us was made in the way described in an earlier paper.[2] In our first experiment 2 grams of the quinone were dissolved in methyl alcohol, and allowed to stand for two weeks at ordinary temperatures in a corked flask, when a yellowish white substance was obtained, which contained an amount of chlorine corresponding to the formula $(C_6Cl_4O_2)_2CH_3OH$. As it melted with reddening, it seemed to be the α-body corresponding to the derivative of tetrabromorthoquinone described by Porter and one of us,[3] but we have never succeeded in obtaining this compound again, although we have tried numerous experiments with all the variations in conditions that we could devise. We do not feel justified, therefore, in assuming its existence on the strength of a single analysis.

Our attempts to prepare the α-compound, although unsuccessful, made us acquainted with the effect of different conditions on the products of the reaction. Thus we found, when working in the cold, if the amount of methyl alcohol was from 1–5 cc. for each gram of quinone, the first product was usually the β-compound, $(C_6Cl_4O_2)_2CH_3OH$, melting at 157°, accompanied by a little of a white substance melting at 218°, the hexachlororthomethylhemiacetalpyrocatechin ether, while

[1] THIS JOURNAL, **34**, 460 (1905).
[2] *Ibid.*, **37**, 11 (1907).
[3] *Ibid.*, **31**, 97 (1904).

from the mother liquors were obtained trichlororthoxyparaquinone, melting at 198° and chloranilic acid.

If 8 to 12 cc. of alcohol were used to 1 gram quinone, after 6–8 days the product was almost entirely trichlormethoxyorthoquinonemonohemiacetal, melting at 138°–140°, but, if the mixture was allowed to stand for two weeks longer, this hemiacetal was replaced by the hexachlororthomonomethylhemiacetal-pyrocatechin ether, melting at 198° and a little of the corresponding complete hemiacetal melting at 218°.

The effect of changes of temperature on the reaction was also studied. A solution of 1 gram of quinone in 2 cc. of methyl alcohol was heated on the steam bath for half an hour, and then allowed to stand at ordinary temperatures for 4–5 days. The only difference here was that the compound melting at 218° did not appear, but the one melting at 138°–140° was formed, the other products being, as in the cold, the β-compound and the trichloroxyparaquinone. On the other hand, a solution of 1 gram of quinone in 8 cc. of methyl alcohol was allowed to stand at the temperature of melting ice; in this case the only product was the compound melting at 138°–140°, which was formed in 30 days instead of in 6–8 as at ordinary temperatures. As these experiments gave no new compounds we did not think it worth while to study variations of temperature more carefully.

Octochlororthoquino-1-methoxy-1′-hydroxy-1,2,2-trioxide, β-Methyl Addition Compound, $C_6Cl_4OCH_3O_3HOC_6Cl_4$.—This substance was formed by the action of methyl alcohol on tetrachlororthobenzoquinone in the cold, when for each gram of the quinone 1 or 2 cc. of the alcohol were used. After the mixture had stood 6–7 days in a corked flask, a deposit of white rhombic crystals was obtained, which were washed with cold methyl alcohol, and recrystallized from benzene, until they showed the constant melting point 157°, when the substance was dried at 100° for analysis. Hydrochloric acid was always present in the filtrate from the crude β-compound, but this undoubtedly owed its formation to secondary reactions, to be considered later.

I. 0.1770 gram substance gave 0.3840 gram AgCl.

II. 0.1853 gram substance gave 0.4044 gram AgCl.
III. 0.2502 gram substance gave 0.5472 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2CH_2OH$.	Found. I.	II.	III.
Cl	54.19	53.63	53.95	54.07

Properties of Octochlororthoquino-1-methoxy-1′-hydroxy-1,2,2-trioxide.—It crystallizes from benzene in white, rhombic plates, which melt at 157° without any apparent decomposition. It is easily soluble in benzene; slightly soluble in ether, chloroform, ethyl acetate, ligroin, or toluene, very slightly soluble in methyl alcohol. The three strong mineral acids have no effect on it and the same is true of potassic hydrate in aqueous solution, but fusion with potassic hydrate decomposes it completely. By reducing the strength of the alkali a brown substance was formed, which may be worth further investigation. With fuming nitric acid it formed oxalic acid and a small amount of a yellow oil, which gave up chloranilic acid to sodic hydrate, and then became colorless. Hydrochloric acid converted this oil when the two were heated together, into two products, white rhombic plates, melting at 104°, and long white needles, melting at 185°. In another experiment in which the nitric acid contained some argentic nitrate trichloroxyparaquinone was formed. It is possible that the study of some of these substances made by fuming nitric acid would throw light on the structure of the β-compounds, but the yields are so small that the work would be very laborious.

That this substance belongs to the β-series is shown by its crystallizing in white rhombic plates, which melt without reddening and by its marked stability. The constitution of these β-compounds has been discussed in an earlier paper.[1]

3,5,6-Trichlor-4-methoxyorthobenzoquinonemonohemiacetal, $C_6Cl_3OCH_3OOCH_3OH$.—When one gram of tetrachlororthobenzoquinone was dissolved in 8–12 cc. of methyl alcohol, and allowed to stand at ordinary temperatures for 6–8 days, the product was principally this monohemiacetal which crystallized in white, rhombic plates when the solution was allowed to evaporate spontaneously. It was also obtained from the mother liquors of the β-compound formed by the action of one gram of quinone with 5 cc. of the

[1] This Journal, 37, 87 (1907).

alcohol, and by heating such a solution on the steam bath for an hour and then allowing it to stand in the cold for 4–5 days, but both these methods gave smaller yields and much more impure products than the first.

It was purified by washing with a mixture of 5 parts of ligroin to 1 of benzene, and crystallization from a mixture of equal parts of these two solutions or from benzene alone, three or four crystallizations being usually sufficient. It was dried *in vacuo* for analysis.

I. 0.2395 gram substance gave 0.3161 gram CO_2 and 0.0776 gram H_2O.

II. 0.1981 gram substance gave 0.3079 gram AgCl.

III. 0.2087 gram substance gave 0.3272 gram AgCl.

IV. 0.2297 gram substance gave 0.3646 gram AgCl.

V. 0.2215 gram substance gave 0.3553 gram AgCl.

	Calculated for $C_6Cl_3OCH_3OOCH_3OH$.	Found. I.	II.	III.	IV.	V.
C	35.10	35.99	....	....	....	....
H	2.56	3.60	....	....	....	....
Cl	38.94	....	38.43	38.77	39.23	39.66

Molecular weight determinations by the boiling point method gave the following results:

I. 0.2965 gram substance dissolved in 32.25 grams benzene, gave Δ 0°.087.

II. 0.4117 gram substance, dissolved in 31.95 grams benzene, gave Δ 0°.123.[1]

	Calculated for $C_6Cl_3OCH_3OOCH_3OH$.	Found. I.	II.
Mol. wt.	273.5	275.7	273.3

Properties of the 3,5,6-Trichlor-4-methoxyorthoquinonemonomonomethylhemiacetal. — It crystallizes from benzene in thick rhombic plates of a creamy white color. It melts at 138°–140° to a colorless liquid, which quickly changes to a faint brown, and becomes red after standing in the hot bath for 5 or more minutes. It is easily soluble in ethyl or methyl alcohol, ether, ethyl acetate, acetone, chloroform, benzene, toluene, or glacial acetic acid; slightly soluble in ligroin, or in hot water, which

[1] The constant used was 26.1: Beilstein's Handb. Supp., p. 2.

gives a characteristic purple solution. Strong hydrochloric acid when heated converts it into the oxyparaquinone, $C_6Cl_3OHO_2$, and the same change is brought about by warming it with phosphoric oxychloride. Strong nitric acid or strong sulphuric acid dissolves it, forming a brilliant red liquid; sodic hydrate, in the cold, gives an orange color, while on heating sodic chloranilate is formed. Methyl alcohol, at ordinary temperatures, had no action on it, even after the solution had stood for several weeks, but a specimen of it which had been in contact with water for five months was decomposed.

On one occasion, when a methyl alcohol solution of the hemiacetal was treated with a few drops of dilute hydrochloric acid, and shaken for about ten seconds, fine yellow needles separated, which, after crystallization from benzene, melted with decomposition at 210°. A single analysis of an insufficient amount of this substance dried *in vacuo* indicated that it was dimethoxydichlororthoquinone.

0.0479 gram substance gave 0.0573 gram AgCl.

	Calculated for $C_6Cl_2(OCH_3)_2O_2$.	Found.
Cl	29.95	29.58

But it is obvious that its existence cannot be considered established, until it is supported by more analyses with larger amounts of substance. Unfortunately all our attempts to make it again proved fruitless, so we must content ourselves with this preliminary account of it. It was soluble in all the common organic solvents, in acids, and in alkalies giving yellow solutions.

3,5,6-Trichlor-4-methoxyorthoquinone-monoacetmethylacetal, $C_6Cl_3(OCH_3)O(OCH_3OC_2H_3O)$.—Two grams of the hemiacetal melting at 138°–140° were heated with 20 cc. of acetic anhydride, under a return condenser, on the water bath, for half an hour. On cooling, the product crystallized out and was purified by three crystallizations from a mixture of benzene and ligroin, when it showed the constant melting point 149°–150°. It was dried at 100° for analysis.

0.1857 gram substance gave 0.2549 gram AgCl.

	Calculated for $C_6Cl_3(OCH_3)O(OCH_2OC_2H_5O)$.	Found.
Cl	33.76	33.93

Properties.—It crystallizes from the mixture of equal parts of benzene and ligroin in semitransparent white prisms; from methyl alcohol in rectangular prisms, which melt at 149°–150° to a colorless liquid. It is very soluble in acetone, ethyl acetate, benzene, or toluene; soluble in hot ether; slightly soluble in hot ethyl alcohol; more soluble in hot methyl alcohol; insoluble in water. Strong hydrochloric acid, or strong nitric acid shows no apparent action with it; strong sulphuric acid gives a red solution with it; sodic hydrate forms an orange solution when hot, which deposits orange tapering needles on cooling.

3,5,6-Trichlor-4-methoxyorthoquinone-monoacetmethylacetalhydrazone, $C_6Cl_3OCH_3(OCH_3OC_2H_3O)N_2HC_6H_5$.—One gram of the methylacetacetal melting at 149°–150° was mixed with 10–12 cc. of phenylhydrazine, and after warming the mixture for a few minutes on the steam bath it was allowed to stand over night. The product was washed with toluene to free it from a dark reddish brown liquid, and attempts were made to purify the grayish needles thus obtained by crystallization, but it was found that all the common solvents decomposed the substance if heated with it, except a mixture of benzene with a large excess of ligroin, and this barely dissolved it. Accordingly it was prepared for analysis by washing thoroughly with toluene, benzene mixed with ligroin, alcohol, and ether, after which it was dried *in vacuo*.

0.1492 gram substance gave 0.1572 gram AgCl.

	Calculated for $C_6Cl_3(OCH_3)_2OC_2H_3ON_2HC_6H_5$.	Found.
Cl	26.26	26.05

Properties.—The hydrazone forms silvery gray needles which melt at 235° sharply to a faint brown liquid. It dissolves in alchool, or benzene to a red liquid which deposits a red substance; it is very slightly soluble in all the other common solvents, when cold, and is decomposed, when heated with them. Acids and alkalies dissolve it with decomposition.

3,5,6-Trichlor-2-oxyparabenzoquinone, $C_6Cl_3OHO_2$.—This sub-

stance is most conveniently obtained from the orthohemiacetal, $C_6Cl_3OCH_3O(OCH_3OH)$, melting at 138°–140°, by the action of hydrochloric acid. The reaction takes place in open vessels even in the cold, but it is more conveniently carried on at a gentle heat. The product was nearly pure, two crystallizations from a mixture of one part of benzene with one of chloroform raising the melting point to 198°, where it remained constant.

It was also formed by the action of 2 cc. of methyl alcohol on 1 gram of tetrachlororthoquinone. In three experiments this substance was apparently deposited before the β-compound, and in all our preparations of the β-compound it seemed also to be produced, and was isolated from the mother liquors as follows: The thick dark red syrup obtained by driving off the solvent was treated with a small quantity of chloroform, and vigorously stirred, scratching the sides of the vessel with the rod which led to the separation of orange plates. The mass of syrup and crystals was then freed from part of the impurity by extraction with a mixture of equal parts of benzene and chloroform, and the very impure product purified by crystallization from a similar mixture. It was hard to remove the last traces of impurity, but after 36 crystallizations, the compound melted constant at 198°. The substance in whatever way prepared was dried *in vacuo* for analysis.

I. 0.1793 gram substance gave 0.2082 gram CO_2 and 0.0266 gram H_2O.

II. 0.2063 gram substance gave 0.2375 gram CO_2 and 0.0366 gram H_2O.

III. 0.1491 gram substance gave 0.2845 gram AgCl.

IV. 0.1607 gram substance gave 0.3062 gram AgCl.

	Calculated for $C_6Cl_3OHO_2$.	Found. I.	II.	III.	IV.
C	31.65	31.66	31.39	....	....
H	0.44	1.65	1.97	....	....
Cl	46.82	....	....	47.18	47.11

Properties of 3,5,6-trichlor-2-oxyparaquinone.—It crystallizes from equal parts of benzene and chloroform in hexagonal orange plates with a brilliant lustre, which seem to undergo

a slight decomposition on exposure to the air, as the crystals turn purplish black probably from the action of the ammonia in the air of the laboratory. It melts, if heated in the bath at 198° to a pale brown liquid; but, if instead the bath was heated to 202°–203° and the tube containing the substance then introduced, the crystals did not melt for 30 seconds. Zincke and Schaum[1] give its melting point as 194°. It dissolves in ethyl alcohol, methyl alcohol, or water with a purple color; the aqueous solution shows no signs of decomposition in the cold, but, if evaporated to dryness on the steam bath, a dark carbonaceous residue is left. It is easily soluble in ether, ethyl acetate, chloroform, acetone, benzene, or toluene; less soluble in ligroin. Hot hydrochloric acid dissolves it, and deposits it unaltered on cooling; strong nitric acid or sulphuric acid dissolves it with decomposition; fuming nitric acid forms oxalic acid; sodic hydrate in the cold forms an orange solution with it, which on heating turns purple, and deposits reddish purple needles of sodic chloranilate; ammonic hydrate gives a dark purple solution which deposits black needles not decomposed below 300°. From the color of this ammoniacal solution it would be inferred that it contained ammonic chloranilate, but with certain reagents it gave different results from those with the chloranilate while with others the precipitates were of the same color. The most marked differences were, with nickel, purple instead of grass-green; with manganese no precipitate instead of a dark brown one; with zinc no action instead of a pinkish white flocculent precipitate; with bismuth dark green instead of dark blue. These differences justify to a certain extent the assumption that the liquid contains at least some of the ammonium salt of the oxyparaquinone.

3,5,6-Trichlor-2-acetoxyparaquinone, $C_6Cl_3OC_2H_3OO_2$. — One gram of the 3,5,6-trichlor-2-oxyparaquinone was heated on the steam bath for half an hour under a return condenser with 10 cc. of acetic anhydride, when on cooling brass colored crystals were deposited, which were crystallized three times from equal parts of benzene and chloroform, after which they showed the constant melting point 127°, and were dried at 100° for analysis.

[1] Ber. d. chem. Ges., **27**, 556 (1894).

0.1408 gram substance gave 0.2262 gram AgCl.

	Calculated for $C_6Cl_3OC_2H_3O_2$.	Found.
Cl	39.52	39.72

Properties.—It crystallizes from a mixture of benzene and chloroform in diamond-shaped yellow plates with a brassy lustre, which melt at 127°. It is very soluble in ether, acetone, chloroform, or toluene; much less soluble in alcohol, or benzene; slightly soluble in ligroin or water. The aqueous solution has the characteristic purple color of all the members of this class of compounds. Hydrochloric acid dissolves it when hot with an orange color; nitric acid also gives an orange solution; sulphuric acid a red one; sodic or ammonic hydrate dissolves it with a purple color.

3,5,6-Trichlor-2-aceloxy-1-4-dioxybenzene, $C_6Cl_3OC_2H_3O(OH)_2$. —Two grams of the acetyl compound just described, melting at 127°, mixed with 20 cc. of water were treated with gaseous sulphurous dioxide for an hour, when white needles were formed which, after three crystallizations from equal parts of benzene and ligroin, showed the constant melting point 155°, when the substance was dried *in vacuo* for analysis.

0.1507 gram substance gave 0.2423 gram AgCl.

	Calculated for $C_6Cl_3OC_2H_3O(OH)_2$.	Found.
Cl	39.23	39.75

Properties.—It crystallizes from benzene and ligroin in white needles arranged in circular radiating groups, and melts at 155°. It is easily soluble in alcohol, ether, chloroform, ethyl acetate, or acetone; moderately soluble in benzene, or toluene; slightly soluble in ligroin; dissolves in hot water with a pale purple color. Strong hydrochloric acid does not affect it; nitric acid or sulphuric acid dissolves it with decomposition; sodic hydrate gives a dark green solution; ammonic hydrate a greenish brown. It did not give the pyrocatechin reactions with ferric chloride, plumbic acetate, or picric acid.

Reduction of Trichloroxyparaquinone.—Two grams of the oxyparaquinone melting at 198°, mixed with a little water, were

treated with gaseous sulphurous dioxide, which decolorized it in two minutes forming grayish white crystals. These, after recrystallization from equal parts of benzene and chloroform, melted at 162°, and were dried at 100° for analysis.

0.1972 gram substance gave 0.3730 gram AgCl.

	Calculated for $C_6Cl_3(OH)_3$.	Found.
Cl	46.41	46.77

This substance should be the 3,5,6-trichloroxyhydroquinone but, as Zincke and Schaum found it melted at 160°, we thought it necessary to make the acet compound of our product in order to establish its identity. For this purpose 1 gram of it was allowed to stand with 10 cc. of acetic anhydride over night. The white product thus obtained crystallized from equal parts of benzene and ligroin in radiating groups of white needles with tapering ends, which melted at 171°, the melting point found by Zincke and Schaum[1] for 3,5,6-trichloroxyhydroquinone triacetate. For greater certainty it was analyzed.

0.1516 gram substance gave 0.1860 gram AgCl.

	Calculated for $C_6Cl_3(OC_2H_3O)_3$.	Found.
Cl	29.96	30.33

Chloranilic Acid, $C_6Cl_2(OH)_2O_2$.—This substance was one of the products when 1 gram of tetrachlororthoquinone stood in the cold for three months with 1 cc. of methyl alcohol. It was extracted from the residue left on evaporating the mother liquors from the β-compound by treating it with a mixture of equal parts of benzene and chloroform, in which it is insoluble, and was purified by crystallization from methyl alcohol and petroleum ether, when it separated in long, red, tapering needles at the point of contact of the liquids. After five crystallizations it was dried at 100° for analysis.

The same compound was more easily obtained by the action of potassic hydrate on the oxyparaquinone, melting at 198°.

I. 0.2086 gram substance gave 0.2638 gram CO_2 and 0.0275 gram H_2O.

[1] Ber. d. chem. Ges., **27**, 559 (1894).

II. 0.1560 gram substance gave 0.2162 gram AgCl.
III. 0.1594 gram substance gave 0.2200 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	Found. I.	II.	III.
C	34.43	34.49	....	....
H	0.95	1.47	....	....
Cl	33.97	....	34.27	34.12

These analyses showed that the substance had the composition of chloranilic acid, and it was proved to be this substance instead of an isomer of it by a careful comparison of our product with chloranilic acid made from chloranil, which established the complete identity of the compounds. The details of this comparison have been given in an earlier paper;[1] it is enough here, therefore, to say that it included the analyses of the following substances: $C_6Cl_2(OH)_2O_2.2H_2O$, $C_6Cl_2(OK)_2O_2.H_2O$, $C_6Cl_2(ONa)_2O_2.3H_2O$, $C_6Cl_2O_2BaO_2.3H_2O$; the ammonium salt of each acid gave the same characteristic precipitates with various reagents,[1] and the dimethylether of our acid from tetrachlororthoquinone melted at 141°–142°, the melting point given by Kehrmann[2] for the dimethylether of chloranilic acid.

Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether, $C_6Cl_4O_2.C_6Cl_2O(OCH_3OH)$.—(1) This compound was obtained by the action of 8 cc. of methyl alcohol on 1 gram of tetrachlororthoquinone. After the mixture had stood at ordinary temperatures for 6–8 days, the trichlormethoxyorthoquinonemonohemiacetal, melting at 138°–140°, was formed, but, if the mixture was allowed to stand 6–8 days longer, the new product was deposited crystallizing in pyramids. This was washed with cold methyl alcohol, and then recrystallized three times from a mixture of equal parts of benzene and ligroin, when it showed the constant melting point 198°. Analysis II.

(2) Equal weights of the monohemiacetal, melting at 138°–140° and tetrachlororthoquinone were dissolved in methyl alcohol and allowed to stand in a corked flask at ordinary temperatures. After 4–5 days the hexachlor compound melting at 198° was formed. Analysis III.

[1] This Journal, **37**, 98 (1907).
[2] J. prakt. Chem. [2], **40**, 370 (1889).

(3) Two grams of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, were allowed to stand with 15 cc. of methyl alcohol at ordinary temperatures. In 24 hours the brilliant red color of the ether began to fade, and at the end of a week the solid had turned yellow. After three crystallizations from equal parts of benzene and ligroin it melted constant at 198°. Analysis IV.

I. 0.2148 gram substance gave 0.2727 gram CO_2 and 0.1008 gram H_2O.

II. 0.1483 gram substance gave 0.2836 gram AgCl.

III. 0.1570 gram substance gave 0.2984 gram AgCl.

IV. 0.1373 gram substance gave 0.2587 gram AgCl.

	Calculated for $C_6Cl_4O_2.C_6Cl_2O(OCH_3OH)$.	Found. I.	II.	III.	IV.
C	34.43	34.62	...	...	...
H	0.88	5.21	...	...	...
Cl	47.02	...	47.28	46.92	46.51

A second combustion gave results which did not agree with this and unfortunately it was made so late that there was no time to prepare a fresh sample of the substance.

A molecular weight determination by the boiling point method gave the following result:

0.3214 gram substance, dissolved in 26.33 grams C_6H_6, gave $\Delta = 0°.073$.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.	Found.
Mol. wt.	453	436.3

The trichloroxyparaquinone, $C_6Cl_3OHO_2$, described earlier, melts at the same temperature, 198°, and contains nearly the same amount of chlorine as this substance, but that they are not identical is shown by this molecular weight determination, the percentage of carbon, and a comparison of the properties of the two substances, which is given in the introduction.

Properties of Hexachlororthoquinomethylmonohemiacetalpyrocatechin ether.—It crystallizes from alcohol in long tapering delicate yellow needles, which are arranged in rosettes, when the solvent used is benzene and ligroin. It melts at 198° to a red

liquid. It is soluble in alcohol or methyl alcohol; easily soluble in ether, acetone, ethyl acetate, benzene, or toluene. Strong hydrochloric acid has no effect on it; strong nitric acid gives a cream-colored product; fuming nitric acid the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, as does also strong sulphuric acid; sodic hydrate gives a yellow solution, soon passing into sodic chloranilate; ammonic hydrate gives a purple solution.

Action of Sulphuric Acid on the Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether. — One gram of the compound when mixed with strong sulphuric acid gave but a slight reaction in the cold, but upon heating the red ether was formed in a few minutes. This was recognized by its color, melting point 298°–300°, and the following analysis:

0.1765 gram substance gave 0.3623 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.75

A quantitative determination of the amount of ether formed gave the following result:

0.3642 gram of the yellow compound gave 0.3344 gram $C_{12}Cl_6O_4$ instead of 0.3385 calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.

Action of Methyl Alcohol and Hydrochloric Acid on the Monohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.— One gram of the substance mixed with 15–20 cc. of methyl alcohol and a few drops of hydrochloric acid stood for three months at ordinary temperatures and was converted completely into the hexachlororthoquinohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, described later, which was recognized by its melting point, 218°, and the following analysis:

0.1864 gram substance gave 0.3333 gram AgCl.

	Calculated for $C_{14}Cl_6O_6H_8$.	Found.
Cl	43.92	44.21

In another experiment, which differed from the preceding only in the fact that the mixture was boiled for an hour before being set aside to stand for four months, the result was different, chloranilic acid being formed and a substance melting at 190°, which was probably tetrachlorpyrocatechin.

Action of Acetic Anhydride on the Monohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—One gram of the substance was heated with 15 cc. of acetic anhydride on the steam bath under a return condenser. After about 20 minutes a quantity of the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, separated, but if the heating was continued for 2 hours the only product was a yellow substance, which, after four crystallizations from equal parts of benzene and ligroin, melted constant at 215°, when it was dried at 100° for analysis.[1]

0.1697 gram substance gave 0.2949 gram AgCl.

	Calculated for $C_{12}Cl_6O_4(C_2H_3O)_2$.	Found.
Cl	42.01	42.95

Properties.—It crystallizes from benzene and ligroin in masses resembling a cauliflower, which are deep yellow at the centre shading into a silvery white on the edges. It melts at 215° to a light brown liquid, and is soluble in alcohol, methyl alcohol, ether, acetone, ethyl acetate, or benzene; much less soluble in ligroin. Strong hydrochloric acid, when heated to 140° with it in a sealed tube for five hours, converted it into an orange-brown product melting in the crude state at 180°, and the orange acid solution deposits orange needles, which dissolve in water with a purple color. Strong nitric acid has no apparent effect on it, hot; strong sulphuric acid gives the red hexachlor ether; alkalies dissolve it slightly.

Hexachlordiacetoxypyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O_2(C_2H_3O)_2$. —This substance was made for comparison with that just described. The red hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$, was reduced with granulated zinc and acetic acid, and the dihydroxy ether thus obtained crystallized from alcohol, until it showed the melting point 290°, when for further security it was dried at 100°, and analyzed.

0.1170 gram substance gave 0.2369 gram AgCl.

	Calculated for $C_{12}Cl_4O_4H_2$.	Found.
Cl	50.36	50.06

[1] Later experiments have shown that this substance is $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.

One gram of this reduced ether was heated with 12–15 cc. of acetic anhydride on the steam bath, under a return condenser for half an hour. On cooling, the product crystallized in pure white plates, which, after three crystallizations from equal parts of benzene and ligroin, showed the constant melting point 282°, when it was dried at 100° for analysis.

0.1537 gram substance gave 0.2625 gram AgCl.

	Calculated for $C_{12}Cl_8O_4(C_2H_4O)_2$.	Found.
Cl	42.01	42.22

Properties of Hexachlordiacetoxypyrocatechin Ether.—It crystallizes in spherical masses of glistening white leaflets, which melt at 282°, forming a colorless liquid. It is easily soluble in chloroform, benzene, or toluene; slightly soluble in alcohol, ether, ethyl acetate, or ligroin. When heated to 140° in a sealed tube, for five hours with 5 cc. of strong hydrochloric acid, it formed a grayish brown crystalline product, which melts without purification, at 285°. Strong nitric acid has no visible effect; hot strong sulphuric acid gives a brown product; alkalies have no action on it.

The red ether, $C_6Cl_4O_2C_6Cl_2O_2$, when boiled for five hours with acetic anhydride, gave a product, which, after two crystallizations from a mixture of benzene and ligroin, melted at 280°–282°, and showed a pale fawn color. There seems no doubt, therefore, that this product is identical with that from the reduced ether just described.

A comparison of this compound with the acet derivative of the monohemiacetal will be found in the introduction.

Hexachlororthoquinomethylhemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.—This compound was formed by the action of methyl alcohol on tetrachlororthoquinone in the cold, no matter what might be the concentration, but more of it seemed to be formed with strong than with dilute solutions. It was separated from the other products by fractional crystallization, the separation from the β-compound being accomplished with methyl alcohol.

This body was more conveniently prepared from the dark

red syrupy residue obtained by evaporating the mother liquors from the β-compound (dilutions of 1:5 or less). This was dissolved in methyl alcohol and a little hydrochloric acid, and after standing for 4–5 days in a corked flask, at ordinary temperatures, white plates separated, which were crystallized from benzene till they showed the constant melting point 218°.

It was also formed as shown by its melting point, 218°, and an analysis (IV), when a pure specimen of the trichloroxyparaquinone, melting at 198°, dissolved in methyl alcohol and mixed with a little hydrochloric acid, was allowed to stand six months at ordinary temperatures.

As already stated, the hexachlororthoquinomonohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, was also converted into this substance by standing for several months with methyl alcohol and a little hydrochloric acid (Analysis V). The products from these various reactions were purified for analysis by crystallization from benzene, and were dried at 100°.

I. 0.1731 gram substance gave 0.2228 gram CO_2 and 0.0486 gram H_2O.

II. 0.1864 gram substance gave 0.3338 gram AgCl.

III. 0.1776 gram substance gave 0.3167 gram AgCl.

IV. 0.1604 gram substance gave 0.2877 gram AgCl.

V. 0.1864 gram substance gave 0.3333 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.	Found.				
		I.	II.	III.	IV.	V.
C	34.64	35.10	. .	. .	. .	. .
H	1.65	3.12	. .	. .	. .	.
Cl	43.92		44.27	44.09	44.34	44.21

The molecular weight was also determined by the boiling point method.

0.3667 gram substance, dissolved in 31.19 grams C_6H_6, gave $\Delta = 0°.043$.

	Calculated for $C_{14}Cl_8O_8H_8$.	$C_{21}Cl_{12}O_{12}H_{12}$.	Found.
Mol. wt.	485	724.5	713.6

According to this result the substance has a molecular weight about one and a half times as great as that assigned to it by our formula, but as we have not succeeded in constructing any

formula with this molecular weight, which would explain the quantitative conversion of the compound into the ether, $C_6Cl_4O_2C_6Cl_2O_2$, by sulphuric acid, we therefore, feel obliged to doubt this molecular weight determination, and to accept provisionally the formula $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, which explains all the relations of this compound. We regret exceedingly that an accident prevented us from carrying out our intention of repeating the molecular weight determination in this case in order to remove the doubt, which must now be felt about the true formula of this substance.

Properties of Hexachlororthoquinohemiacetalpyrocatechin Ether.—It crystallizes from benzene, chloroform, or acetone in diamond-shaped, white plates; from alcohol in glistening leaflets; from ether or ligroin in needles. It melts at 218° to a pale fawn colored liquid, which turns red, when heated to a higher temperature. It is soluble in all the common organic solvents. Strong hydrochloric acid, when heated with it for two hours, with a return condenser, takes on an orange color and deposits orange needles, but most of the substance does not dissolve, and turns chocolate-brown, showing also the other properties of the hexachlordihydroxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$. That it is this body was confirmed by its conversion into the red orthoquino-ether by nitric acid. Nitric acid dissolves the hemiacetal without change of color. Strong sulphuric acid gives the orthoquino ether, $C_6Cl_4O_2C_6Cl_2O_2$, as will be described below. Sodic hydrate dissolves it, giving at first a light yellow solution, which, on acidification, deposits a few orange crystals. By further action sodic chloranilate is formed, which was identified by the properties of the chloranilic acid set free from it by an acid. Ammonic hydrate forms a purple solution with it.

Action of Sulphuric Acid on the Hemiacetal, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.—The hemiacetal (0.8820 gram), melting at 218°, was gently warmed with strong sulphuric acid. When the solid had turned red, the acid was washed out, and the hexachlororthoquinopyrocatechin ether dried and weighed.

	Calculated for $C_{14}Cl_6O_6H_8$.	Found
$C_{12}Cl_6O_4$	0.7635	0.7403

The slight difference between the amounts calculated and found is accounted for by a trifling secondary reaction, which was shown by the faint purple color of the filtrate, and the fact that it gave a reaction for hydrochloric acid. That the insoluble product was the orthoquinoether was proved by its color, crystalline form, solubilities, and the following analysis:

0.1895 gram substance gave 0.3881 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2O_2$.	Found.
Cl	50.59	50.63

Other Reactions of the Hemiacetal.—One gram of the hemiacetal, melting at 218°, was warmed gently with acetic anhydride, and then allowed to stand at ordinary temperatures for four hours. The product after crystallization from ligroin formed cream colored prisms melting at 200°, and was dried at 200°.

0.2172 gram substance gave 0.3842 gram AgCl.

	Found.
Cl	43.73

This is very nearly the amount of chlorine (43.92) in the original substance. It looked, therefore, as if no reaction had taken place.

Phosphoric oxychloride converted the hemiacetal into hexachlororthoquinopyrocatechin ether, recognized by its properties, and melting point 298°–300°.

Reduction with granulated zinc and acetic acid gave in half an hour a product with the properties of hexachlordihydroxypyrocatechin ether.

Methylalcohol, acting in the cold for eight months, converted it partially into chloranilic acid and an unidentified body crystallizing in white needles. If hydrochloric acid was also present, the change took place in half the time

Conversions of Trichloroxyparaquinone into Orthoquinone Derivatives.—In three preparations of the β-compound with 2 cc. of methyl alcohol and tetrachlororthoquinone, after the mixture had stood for 7–8 days, orange plates were deposited, which had the color and crystalline form of the trichloroxyparaquinone, but, if these were allowed to stand with the mother liquors for 24

hours longer they were replaced by white rhombic plates of the β-compound which gave the following result on analysis:

0.2502 gram substance gave 0.5472 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2CH_3OH$.	Found.
Cl	54.19	54.07

We feel no doubt that the orange plates were the oxyparaquinone, $C_6Cl_3OHO_2$, but it does not follow necessarily from these experiments that the β-compound was formed from it, as it may have owed its origin to some other substance contained in the mother liquors. To determine, therefore, whether an orthoquinone derivative could be formed from the oxyparaquinone, as seemed to be the case in these experiments, two grams of a pure sample of the para compound, $C_6Cl_3OHO_2$, melting at 198°, were dissolved in 15 cc. of methyl alcohol, and a little strong hydrochloric acid added. The mixture stood at ordinary temperatures in a corked flask for six months, at the end of which time white crystals were obtained melting at 218°, crystallizing in diamond-shaped white plates, and giving the following result on analysis:

0.1604 gram substance gave 0.2877 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OCH_2OH)_2$.	Found.
Cl	43.92	44.34

There can be no doubt, therefore, that it is the hexachlororthoquinomethylhemiacetalpyrocatechin ether, and it was formed in this case instead of the β-compound because we used a larger proportion of methyl alcohol than that from which the β-product is to be expected. A discussion of the strange nature of this conversion will be found in the introduction.

When the methyl alcohol and hydrochloric acid were heated with the quinone on the steam bath for a long time, chocolate-brown plates were obtained which did not melt below 300°, and gave the following result on analysis:

0.1754 gram substance gave 0.2997 gram AgCl.

	Found.
Cl	42.24

More analytical work is necessary before a formula can be assigned to this substance.

Action of Ethyl Alcohol on Tetrachlororthobenzoquinone.—Ten grams of tetrachlororthoquinone were allowed to stand with 10 cc. of ethyl alcohol in a corked flask, at ordinary temperatures for four months. At the end of two weeks orange yellow crystals had formed, but the whole was allowed to stand for the longer period to make sure that the reaction had run to an end. The crystals were washed with alcohol, and purified by six crystallizations from equal parts of alcohol and benzene, when they showed the constant melting point 210°. Mixed with this yellow principal product were silvery gray needles, which seemed to be the reduced ether, $C_6Cl_4O_2Cl_6Cl_2(OH_2)$, and from the mother liquors trichlor-2-oxyparaquinone, melting at 198°, and chloranilic acid were obtained. If 10 grams of the tetrachlororthoquinone were allowed to stand with 30 cc. of ethyl alcohol (instead of 10 cc.), the same products were obtained except the reduced ether.

Compound melting at 210°.—This substance was dried at 100° for analysis.

I. 0.2112 gram substance gave 0.2814 gram CO_2 and 0.0280 gram H_2O.

II. 0.2019 gram substance gave 0.2688 gram CO_2 and 0.0291 gram H_2O.

III. 0.1882 gram substance gave 0.3489 gram AgCl.

IV. 0.1766 gram substance gave 0.3266 gram AgCl.

V. 0.1718 gram substance gave 0.3185 gram AgCl.

	Calculated for $C_{26}H_{12}Cl_{12}O_{10}$.	Found.				
		I.	II.	III.	IV.	V.
C	35.96	36.34	36.31	...	...	...
H	1.28	1.47	1.60	...	...	...
Cl	45.61	...	...	45.82	45.72	45.83

Analyses I., II. and III. were made with the same preparations IV. and V. from different specimens.

A determination of the molecular weight was made by the boiling point method:

0.4570 gram substance, in 21.86 grams C_6H_6, gave Δ = 0°.060.

	Calculated for $C_{28}H_{12}Cl_{12}O_{10}$.	Found.
Mol. wt.	934	909

These results are sufficient to establish this formula, or one containing 2 atoms less of hydrogen, which would agree equally well with the determinations. We prefer the formula given, because it would be made up by the union of 2 molecules of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, with 2 of ethyl alcohol.

Properties of the Compound Melting at 210° Formed by the Action of Ethyl Alcohol.—It crystallizes in lemon-yellow, diamond-shaped plates, which melt sharply at 210° to a red liquid. It is easily soluble in acetone, ethyl acetate, or benzene; moderately soluble in ether, or chloroform; slightly soluble in alcohol, acetic acid, or ligroin; insoluble in water. Strong hydrochloric acid or nitric acid has no visible effect on it, but fuming nitric acid, when added to the substance dissolved in glacial acetic acid, turns the solution red, and on the addition of water a white precipitate is formed, which melted in the crude state at 202° and seemed to be more soluble than the original substance. Treatment with strong sulphuric acid converts the substance melting at 210° into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, nearly quantitatively.

1.900 grams substance gave 1.7347 grams $C_{12}Cl_6O_4$. Calculated from $C_{28}H_{12}Cl_{12}O_{10}$, 1.713 grams. That this was the red ether was proved by its properties, and the following analysis:

0.1953 gram substance gave 0.4017 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.86

Action of Acetic Anhydride on the Compound Melting at 210°.—One gram of this compound was heated with 15–20 cc. of acetic anhydride on the steam bath, under a return condenser, for 15 minutes, when it was found that a considerable quantity of the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, had been formed, but, if the heating was continued for an hour, this disappeared, and a white product was obtained, which after six crystallizations from equal parts of benzene and ligroin showed the constant melting point 195°, where it was dried at 100°.

0.1643 gram substance gave 0.2810 gram AgCl.

	Calculated for $C_{28}H_{10}(C_2H_3O)_2.Cl_{12}O_{10}$.	Found.
Cl	41.84	42.28

A molecular-weight determination was made by the boiling point method:

0.4228 gram substance dissolved in 33.91 grams C_6H_6 gave $\Delta = 0°.033$.

	Calculated for $C_{28}H_{10}(C_2H_3O)_2Cl_{12}O_{10}$.	Found.
Mol. wt.	1018	986

Properties.—It crystallizes from benzene and ligroin in flat needles with square ends arranged in radiating groups, and is probably white, although portions of our specimens showed a faint purple color. It melts at 195°, and is easily soluble in ether, chloroform, glacial acetic acid, or benzene; slightly soluble in alcohol; very slightly in ligroin. Strong hydrochloric acid, when heated to 140° in a sealed tube with it, gives long, brown needles; strong nitric acid has no effect, but fuming nitric acid gives a reddish brown product; alkalies dissolve it slightly, forming a pale yellow solution.

A specimen of it was heated with sulphuric acid (sp. gr. = 1.41), without any effect so long as it was kept on the steam bath, but upon boiling the acid the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, was formed in a few minutes, which by longer heating was converted into the reduced ether.

Phosphoric oxychloride with or without phosphoric pentachloride at a gentle heat converted the substance melting at 210° into the red ether which was recognized by its properties and the following analysis:

0.1342 gram substance gave 0.2750 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.66

Action of Alkalies with the Compound Melting at 210°.—Two grams of this substance were warmed on the steam bath for a few minutes with a 10 per cent solution of potassic hy-

drate. The dark red needles formed were recrystallized from warm water, and dried to constant weight in the air.

I. 0.1342 gram substance, when heated to 110°, lost 0.0085 gram H_2O.

II. 0.1994 gram substance lost 0.0118 gram H_2O.

	Calculated for $C_6Cl_2(OK)_2O_2.H_2O$.	Found. I.	II.
H_2O	5.94	6.33	5.91

I. 0.1257 gram substance, dried at 110°, gave 0.0772 gram K_2SO_4.

II. 0.1876 gram substance gave 0.1143 gram K_2SO_4.

	Calculated for $C_6Cl_2(OK)_2O_2$.	Found. I.	II.
K	27.37	27.57	27.35

Half a gram of the substance melting at 210° was treated with a 10 per cent solution of sodic hydrate, which gave at first yellow crystals passing easily into purplish red needles, which were recrystallized four times from warm water and dried in the air.

0.1248 gram substance, when heated to 110°, lost 0.0217 gram H_2O.

	Calculated for $C_6Cl_2(ONa)_2O_2.3H_2O$.	Found.
H_2O	17.59	17.39

0.1031 gram salt, dried at 110°, gave 0.0580 gram Na_2SO_4.

	Calculated for $C_6Cl_2(ONa)_2O_2$.	Found.
Na	18.19	18.22

These analyses prove that the salts were chloranilates; and an ammoniacal solution of this body gave, with baric chloride, the characteristic fawn colored precipitate of baric chloranilate.

With more dilute sodic hydrate on one occasion a sky-blue solid was formed, and on another, grayish needles, which seemed to be the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$. In the time at our disposal we have been unable to determine the conditions, which caused these reactions.

Reduction of the compound melting at 210° with granulated

zinc and acetic acid on the steam bath, for half an hour, gave long silky needles, melting at 247°, which by some accident were not analyzed. With nitric acid this product gave the red ether melting at 298°–300°.

0.1057 gram substance gave 0.2192 gram AgCl.

	Calculated for $C_{12}Cl_4O_4$.	Found.
Cl	50.59	51.27

Secondary Products of the Reaction of Ethyl Alcohol on Tetrachlororthoquinone.—The trichlor-2-oxyparaquinone, $C_6Cl_3OHO_2$, was obtained from the mother liquors by allowing the residue from them to stand exposed to the air, until it had partially crystallized, when a little chloroform was added, and the mixture stirred vigorously. It was then treated with a mixture of equal parts of benzene and chloroform, which dissolved the oxyparaquinone, and left the chloranilic acid undissolved. The first substance was purified by recrystallization from benzene and chloroform, till it showed the constant melting point 198°, when it was dried at 100°.

0.1684 gram substance gave 0.3184 gram AgCl.

	Calculated for $C_6Cl_3OHO_2$.	Found.
Cl	46.82	46.74

The chloranilic acid after recrystallization from a mixture of methyl alcohol and petroleum ether sublimed between 285° and 290°, and was dried at 100°.

0.0793 gram substance gave 0.1095 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	Found.
Cl	33.97	34.07

Product Melting at 115°.—If the alcoholic liquid, from which the substance melting at 210° had been deposited, was treated with a small quantity of hydrochloric acid, and allowed to stand at ordinary temperatures for a week, a white product was obtained, which, after washing with cold alcohol and recrystallization from benzene and ligroin, showed the constant melting point 115°, and was dried *in vacuo*.

I. 0.1767 gram substance gave 0.3594 gram AgCl.
II. 0.1708 gram substance gave 0.3417 gram AgCl.

	Found.	
	I.	II.
Cl	50.28	49.48

The analyses were made with specimens from different preparations. This subtance comes very near to trichlorpyrocatechin, $C_6HCl_3(OH)_2$, which contains 49.88 per cent of chlorine, and melts at 115°, when it contains one molecule of water of crystallization; but Cousin,[1] who discovered this compound, found that it loses only half a molecule of water, when dried *in vacuo* and $C_6HCl_3(OH)_2.\frac{1}{2}H_2O$ contains 47.86 per cent of chlorine. He also describes the compound with 1 H_2O as crystallizing in prisms or needles and soluble in alkalies, whereas our product crystallizes in diamond-shaped white plates, and is unaffected by alkalies or acids. With our present data, therefore, it is impossible to settle the nature of this substance definitely. It melts at 115° to a colorless liquid, and is easily soluble in all the common organic solvents.

With a larger quantity of hydrochloric acid the mother liquors gave after three months chloranilic acid and a white product melting at 228°, but formed in insufficient quantity for analysis.

Action of Other Alcohols of the Fat Series on Tetrachlororthoquinone.—Normal propyl alcohol and isoamyl alcohol with tetrachlororthoquinone gave chloranilic acid and oxyparaquinone, $C_6Cl_2OHO_2$, melting at 198°.

I. 0.1597 gram of the red product from normal propyl alcohol gave 0.2215 gram AgCl.

II. 0.1542 gram, from isoamyl alcohol, gave 0.2120 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	Found.	
		I.	II.
Cl	33.97	34.29	33.99

I. 0.1946 gram of the orange product, from normal propyl alcohol, gave 0.3700 gram AgCl.

II. 0.1426 gram, from isoamyl alcohol, gave 0.2715 gram AgCl.

[1] Ann. Chim. Phys. [7], **13**, 483 (1898).

	Calculated for $C_6Cl_3OHO_2$.	Found. I.	II.
Cl	46.82	47.01	47.07

Isopropyl alcohol with tetrachlororthoquinone also gave chloranilic acid and an unidentified brown product.

Tertiary butyl alcohol, on the contrary, gave a product which probably belongs to the β-series. Ten grams of tertiary butyl alcohol were allowed to stand with 10 grams of tetrachlororthoquinone at ordinary temperatures. At the end of two weeks white rhombic plates began to form. These after they had collected in quantity were washed with a mixture of 1 part benzene to 2 of ligroin, and then crystallized from equal parts of benzene and chloroform. After five crystallizations the compound melted constant at 250°, when it was dried at 100° for analysis.

0.1153 gram substance gave 0.2330 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2(CH_3)_2COH$.	Found.
Cl	50.17	49.96

Properties of Octochlororthoquino-1-tertiarybutyloxy-1'-hydroxy-1,2,2-trioxide.—It crystallizes from benzene and chloroform in white rhombic plates, which melt at 250° to a dark liquid. It is easily soluble in ether, acetone, or ethyl acetate; moderately soluble in alcohol, benzene, or chloroform; practically insoluble in ligroin. Strong hydrochloric acid has no effect; strong nitric acid forms a pale brown; strong sulphuric acid a dark brown solution with it; it dissolves in sodic or ammonic hydrate.

Action of Benzyl Alcohol on Tetrachlororthoquinone.—Twenty grams of the quinone were allowed to stand at ordinary temperatures with 20 cc. of benzyl alcohol. In the course of a few hours the red color of the quinone began to disappear, and at the end of 24 hours it was entirely converted into a yellow product, while the liquid had a strong odor of benzyl chloride. The solid product was crystallized from equal parts of benzene and ligroin until it showed the constant melting point 215°, when it was dried for analysis.

I. 0.2958 gram substance gave 0.3655 gram CO_2 and 0.0683 gram H_2O.

II. 0.2249 gram substance gave 0.4572 gram AgCl.
III. 0.2162 gram substance gave 0.4363 gram AgCl.

	Calculated for $C_{13}Cl_6O_4H_2$.	Found. I.	II.	III.
C	34.05	33.69	....	....
H	0.47	2.56	....	....
Cl	50.36	....	50.26	49.89

These analyses show that the substance has a composition very near to that of the dihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, but with our present data we have been unable to assign a definite formula to it. It crystallizes from benzene and ligroin in lemon-yellow square prisms. If the melting-tube containing it is dipped into the hot bath, a constant melting point of 215° is obtained, the substance turning red as it melts; if, instead of this, the substance is heated with the bath, it takes on a faint red at 170°, which becomes deeper as the temperature rises, but it does not melt till 280°. The reason for this behavior is that the hexachlor ether, $C_6Cl_{12}O_4$, begins to form at 170°. It is easily soluble in alcohol, chloroform, acetone, ethyl acetate, or benzene, slightly soluble in ligroin. Boiling with water or very dilute ammonic hydrate converts it into the red hexachlor ether. Strong hydrochloric acid or nitric acid has no effect on it; strong sulphuric acid gives a grass-green color followed by black. Dilute sodic hydrate gives at first the hexachlororthoquino ether, $C_6Cl_{12}O_4$, followed by its decomposition products, chloranilic acid and hexachlordihydroxypyrocatechin ether.

Action of Acetic Anhydride.—Two grams of the substance from benzyl alcohol, melting at 215°, mixed with 10 cc. of acetic anhydride, were warmed on the steam bath under a reverse condenser. After two minutes the solution turned red, and brilliant red crystals were deposited. To be certain that the reaction was complete the mixture was heated for 15 minutes longer, after which the supernatant liquid was poured into an evaporating dish, where it deposited a yellow product. By treating the mass in the flask after the acetic anhydride had evaporated, with dilute alcohol, the red product was obtained in crystals. It was recrystallized from benzene when it formed long, red needles, melting at 298°–300°. This indicated that it was

hexachlororthoquinopyrocatechin ether, which was confirmed by the following analysis of the substance dried at 100°.

0.1768 gram substance gave 0.3609 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.47

It was difficult to purify the yellow product of the reaction, because it was easily soluble in all the organic liquids, and these solutions left it as a thick yellow oil, but by using dilute alcohol we at last obtained it with a constant melting point of 195° when it was dried *in vacuo* for analysis.

I. 0.0800 gram substance gave 0.1635 gram AgCl.
II. 0.1657 gram substance gave 0.3339 gram AgCl.

	Found.	
	I.	II.
Cl	50.53	49.82

The analyses were made from different preparations. We can assign no formula to this substance at present.

Properties.—It crystallizes from dilute alcohol in flocculent needles of a creamy white color, which melt a 195° to a faint brown liquid. It is easily soluble in ether, chloroform, acetone, benzene, or ligroin, somewhat less soluble in alcohol. The best solvent for it is dilute alcohol. Strong hydrochloric acid has no action on it; it is moderately soluble in strong nitric acid; freely soluble in strong sulphuric acid, or alkalies.

A weighed portion of the benzyl alcohol compound was treated with acetic anhydride as already described, and the residue after evaporation of the liquid extracted with dilute alcohol. The residue consisting of hexachlororthoquinopyrocatechin ether was then weighed with the following result:

2.9814 grams substance gave 1.7358 grams $C_{12}Cl_6O_4$.

Reduction of the Benzyl Alcohol Compound.—Two grams of this substance were heated with granulated zinc and acetic acid on the steam bath, when almost at once the liquid turned red, and deposited red crystals, which, after the continuance of the reduction for five minutes, turned chocolate-brown. That this product was the hexachlordihydroxypyrocatechin ether

was shown by its melting point 290°, after recrystallization from alcohol, its other properties and the following analysis:

0.2018 gram substance gave 0.4099 gram AgCl.

	Calculated for $C_{12}Cl_6O_4H_2$.	Found.
Cl	50.36	50.22

Sulphurous dioxide was passed into a mixture of 2 grams of the compound from benzyl alcohol with 50 cc. of water for an hour. The deep yellow color of the original substance faded to a creamy white, after it had stood with the solution of sulphurous acid for 24 hours. It was then recrystallized from a mixture of equal parts of benzene and ligroin, until the gray needles melted at 188°–190° to a black liquid, when it was dried *in vacuo*.

0.2557 gram substance gave 0.5546 gram AgCl.

	Calculated for $C_6Cl_4O_2H_2.H_2O$.	Found.
Cl	53.38	53.62

It would seem, therefore, to be somewhat impure tetrachlorpyrocatechin, which melts at 194°–195° and crystallizes[1] with one molecule of water.

We have been unable to work out a structural formula for the benzyl compound, melting at 215°, from the observations described above, but hope that a further study of its derivatives will throw light on its constitution. When tetrachlororthoquinone was treated with hot benzyl alcohol the product seemed to be the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$.

Action of Tetrachlororthobenzoquinone with Toluene.—

Cold Toluene.—Four products were formed by allowing tetrachlororthoquinone to stand with ordinary toluene at room temperatures.

(1) *Toluene of Crystallization*, $C_6Cl_4O_2.C_7H_8$.—Ten grams of the orthoquinone dissolved in 10 cc. of redistilled toluene were allowed to stand in a corked flask for two days, when long, red needles were deposited, which effloresced rapidly in the air. They were dried quickly on filter paper, and allowed to stand at first in a desiccator, finally *in vacuo*.

[1] Jackson and Boswell: THIS JOURNAL, 28, 529 (1906).

0.6417 gram substance lost 0.1814 gram C_7H_8.

	Calculated for $C_6Cl_4O_2.C_7H_8$.	Found.
C_7H_8	27.22	28.26

The residue was tetrachlororthoquinone.

(2) *α-Water Compound. Octochlororthoquino-1,1′-dihydroxy-1-monoxide*, $C_6Cl_4OOHOHO.C_6Cl_4$.—If the red crystals of tetrachlororthoquinone with toluene of crystallization were allowed to remain in the toluene solution for 10–14 days, they were converted into a pinkish white product.[1] This was washed with a mixture of equal parts of benzene and ligroin, and crystallized from warm benzene, until it showed the constant melting point 172°, when it was dried *in vacuo*.

0.1102 gram substance gave 0.2478 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2H_2O$.	Found.
Cl	55.69	55.59

As it is converted into the hexachlorether, when it melts, it must belong to the α-series.

Properties.—It crystallizes from benzene in white needles arranged in clusters or radiating groups. It melts with reddening at 172°, and is soluble in alcohol, ether, chloroform, acetone, ethyl acetate, or benzene; slightly soluble in ligroin. The three strong acids have no visible effect on it, even when heated with it for a short time; sodic hydrate dissolves it.

(3) *Yellow Product Melting at 290°.*—If instead of removing the α-water compound from its mother liquor as soon as it was formed, it was allowed to remain with it for six weeks; two new products were formed, one yellow, the other chocolate-brown. The yellow substance was washed with ligroin, and then recrystallized four times from equal parts of benzene and ligroin, when it showed the melting point 290°. It was dried *in vacuo*.

I. 0.2267 gram substance gave 0.2764 gram CO_2 and 0.0202 gram H_2O.

II. 0.1492 gram substance gave 0.3167 gram AgCl.

III. 0.1707 gram substance gave 0.3607 gram AgCl.

[1] The mother liquors poured off from this gave the red ether, $C_{12}Cl_8O_4$, when treated with alcohol.

	Calculated for $C_{24}HCl_{13}O_8$.	Found. I.	II.	III.
C	32.79	33.25	....	....
H	0.11	0.99	....	....
Cl	52.53	....	52.48	52.25

The formula given above is one, which might be expected from the conditions of the formation of the substance, since it would be formed by the union of 1 molecule of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, with one of the hemiether, $C_6Cl_4OHOC_6Cl_3O_2$.

Properties.—It crystallizes from benzene and ligroin in rosettes of yellow needles, which on exposure to the air gradually take on a reddish tinge. It melts at 290° to a red liquid, but begins to turn red from the formation of the hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$, at 270°. It is freely soluble in alcohol, ether, chloroform, acetone, ethyl acetate, benzene, or toluene; slightly soluble in ligroin. The three strong mineral acids do not affect it; sodic or ammonic hydrate dissolves it, giving a purple solution. The two products formed by sodic hydrate are sodic chloranilate, and the ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$.

When heated with water, it is converted into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$. A specimen, which had been kept in a corked tube for a year without visible change, was treated with boiling water for some time, so as to make sure that the conversion into the ether was complete with the following result:

0.6277 gram substance gave 0.5820 gram $C_{12}Cl_8O_4$, instead of 0.6017 gram, the calculated amount if the substance is $C_{24}HCl_{13}O_8$.

(4) *Brown Product.*—The brown product of the action of toluene on tetrachlororthoquinone was not obtained in sufficient quantity for analysis. It melted at 182°–183°, and crystallized in fawn-colored needles. As it was soluble in water, gave with ferric chloride a dark green color, and with strong nitric acid a red product, it is probable that it is a substituted pyrocatechin.

Action of Dry Toluene on Tetrachlororthoquinone.—The object of this experiment was to determine whether absolutely dry toluene gave only the compound containing toluene of crystallization. In similar earlier experiments with tetrabrom-

orthoquinone the water compound, $(C_6Br_4O_2)_2H_2O$, had also been obtained, and, as in these cases some care had been taken to dry the toluene, they threw doubt on the composition of the water body in spite of the evidence of the analyses. As these earlier experiments showed that the orthoquinone had a most unusual attraction for water, great pains were taken to exclude it completely from this experiment. The toluene was allowed to stand for eight months in contact with bright metallic sodium, and then distilled *in vacuo*. The quinone was dried at 70° to constant weight, and the glass-stoppered weighing tube selected for the experiment was carefully dried in a current of hot air. Five grams of the quinone were placed in the tube, which was then filled with the toluene as quickly as possible, and the glass stopper replaced leaving only a very small air-bubble in the tube and forcing out some of the solution which evaporating above the junction of the tube and the stopper, assisted in sealing the apparatus. The tube was then allowed to stand in a desiccator over sulphuric acid for six months, so that there might be time for any reaction to take place. At the end of this period the supernatant liquor was poured off into a dry flask, and the toluene driven off by a stream of dry air; the residue was the unaltered quinone. The crystals which had formed in the tube gave up toluene when gently warmed, and also left the unaltered quinone. None of the water compound, therefore, had been formed.

Hot Toluene.—Five grams of tetrachlororthoquinone were heated with toluene on the steam bath, under a return condenser, for six hours, when a yellow product was obtained, which, after recrystallization, showed by its melting point (214°–215° if the substance is dipped into the heated bath) and all its other properties that it was identical with the substance obtained by the action of benzyl alcohol on tetrachlororthoquinone, and this was confirmed by the following analysis.

0.2071 gram substance gave 0.4230 gram AgCl.

Calculated for $C_{12}Cl_4O_4H_2$.	Found.
50.36	50.50

In one experiment hot toluene under the conditions given

above converted the tetrachlororthoquinone into a white product melting at 238°, but we could not obtain this substance again.

Action of Hot Toluene on Tetrabromorthoquinone.—This experiment was tried in the hope that it would throw light on the nature of the chlor compound melting at 215°. Five grams of tetrabromorthoquinone were heated with 5 cc. of toluene (redistilled but not dried) on the steam bath, under a return condenser for an hour. At the end of this time the quinone was wholly converted into a yellow compound, which proved to be the heptabromorthoquinopyrocatechin hemiether, discovered by Russe and one of us.[1] Its identity was established by its melting point, 244°, and the following analysis:

3.0208 gram substance lost 0.3993 gram C_6H_6 when heated to 100°.

	Calculated for $C_{12}HBr_7O_4 1/2C_6H_6$.	Found.
C_6H_6	13.22	13.22

0.1964 gram substance dried at 100° gave 0.3373 gram AgCl.

	Calculated for $C_{12}HBr_7O_4$.	Found.
Br	72.80	73.08

This seems to be the best method yet found for preparing the heptabrom hemiether, as it gives it quickly and in an essentially pure state.

Action of Acetic Acid on Tetrachlororthobenzoquinone.—An experiment in which the quinone was evaporated to dryness several times[2] with glacial acetic acid yielded little except the red ether, $C_6Cl_4O_2C_6Cl_2O_2$. Accordingly the action of cold acetic acid was tried. Ten grams of tetrachlororthoquinone were allowed to stand with 50 cc. of glacial acetic acid in a corked flask for 8 months, when the cream white product was purified by crystallization from glacial acetic acid, followed by washing with alcohol, or by using equal parts of glacial acetic acid and alcohol as the solvent. The melting point was constant at 250°–252°, when the substance was dried at 100° for analysis:

I. 0.1704 gram substance gave 0.3550 gram AgCl.

[1] This Journal, **35**, 165 (1906).

[2] Method of Jackson and Koch: This Journal, **26**, 42 (1901).

II. 0.1471 gram substance gave 0.3057 gram AgCl.
III. 0.1056 gram substance gave 0.2169 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2CH_2COOH$.	Found. I.	II.	III.
Cl	51.45	51.51	51.38	50.78

As the substance turns red on melting it belongs to the α-series.

Properties of the α-Addition-Compound, Octochlororthoquino-1-acetoxy-1'-hydroxy-1-monoxide.—It crystallizes from acetic acid in spherical masses of white needles, which melt at 250°–252° to a red liquid. It is freely soluble in ether, acetone, ethyl acetate, or acetic acid; moderately soluble in alcohol, chloroform, or benzene; slightly soluble in ligroin. The three strong mineral acids have no effect on it; sodic hydrate dissolves it, and if heated with ammonic hydrate for some time it turns brown. An attempt to make the β-compound with acetic anhydride and sodic acetate gave an impure product, which was never brought into a state fit for analysis.

Action of Water on Tetrachlororthobenzoquinone.—Three grams of the orthoquinone were heated with 50 cc. of water on the steam bath. The solution turned dark reddish brown, and in a few minutes a brilliant red product was formed, which, after washing with alcohol and recrystallization from benzene, melted at 298°–300°, and showed the other properties of the hexachlororthoquinopyrocatechin ether.

0.1396 gram substance dried at 100° gave 0.2851 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.49

Two grams of the tetrachlororthoquinone after standing with 100 cc. of water, at ordinary temperatures for two months, gave a white product which was not studied.

Derivatives of Hexachlororthoquinopyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O_2$.

Action of Methyl Alcohol.—Two grams of the ether were allowed to stand at ordinary temperatures in a corked flask with 15 cc. of methyl alcohol. At the end of 24 hours the red color of the ether began to fade, and after seven days the solid had be-

come pale yellow. After three crystallizations from equal parts of benzene and ligroin it melted constant at 198°, to a red liquid.

0.1373 gram substance gave 0.2587 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.	Found.
Cl	47.02	46.58

From this analysis, the pale yellow color, and the fact that it crystallizes in needles, there is no doubt that this substance is the hexachlororthoquinomonohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, described earlier in this paper.

In another experiment tried under similar conditions, except a few drops of water were added to the methyl alcohol, the reaction took place more slowly, but after three months the following products were obtained:

1. The yellow compound, melting at 198°, mentioned above.
2. Hexachlororthomethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, melting at 218°.
3. Choranilic acid.
4. Unidentified light fawn-colored needles.

Action of Ethyl Alcohol.—Three grams of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, were allowed to stand with 20 cc. of ethyl alcohol at ordinary temperatures, for three months. Three products were obtained; (1) an orange body melting at 210°.

0.1981 gram substance gave 0.3769 gram AgCl.

	Calculated for $C_{28}H_{18}Cl_{12}O_{10}$.	Found.
Cl	45.61	47.03

This substance is, therefore, identical with that formed by the action of ethyl alcohol on tetrachlororthoquinone. (2) Chloranilic acid. (3) Unidentified, fawn colored needles.

A yellow substance melting at 210° also seemed to be formed by the action of normal propyl alcohol on tetrachlororthoquinone, but it cannot be identical with that just mentioned, because that is an ethyl compound.

Phenylhydrazine reduced the red ether to hexachlordihydroxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, and therefore,

acted in the same way[1] as with hexabromorthoquinopyrocatechin ether.

CAMBRIDGE, February 28, 1907.

THE OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS IN THE VICINITY OF 5°.[2]

BY H. N. MORSE, J. C. W. FRAZER AND P. B. DUNBAR.

The considerable deviation[3] of osmotic from gas pressure in the vicinity of 0°, while the two were found to be in substantial agreement[4] in the neighborhood of 20°, made it desirable to determine the pressures of both cane-sugar and glucose solutions at several intermediate temperatures, in order to ascertain just where, and at what rate or rates, the divergences observed at low temperatures disappear. Later it will, of course, be necessary to determine whether the agreement between the two, which is observed in the vicinity of 20°, persists at still higher temperatures.

The intervals which have been selected for the former purpose are 5°, 10°, and 15°. These temperatures cannot be exactly maintained on the scale and for the length of time necessary for the measurement of pressure, but sufficiently close approximations to each one of them can be secured at some period of the year through the aid of the hydrant water.

The device by means of which we endeavor to maintain the bath[5] at the temperature of the hydrant water is as follows: A series of connected, vertically-placed, brass pipes, $\frac{1}{4}$ inch in external diameter, 34 inches in length, and two inches apart, is arranged entirely around the four interior vertical walls of the bath. Each pipe extends from a point near the top of the air space to a depth of 15 inches under the water below, except for a short distance in front of the window, where the pipes are

[1] Jackson and Shaffer: THIS JOURNAL, **34**, 466 (1905).

[2] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **33**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558.

[3] *Ibid.*, **37**, 425 and 558.

[4] *Ibid.*, **34**, 1; **36**, 39; **37**, 325.

[5] *Ibid.*, **36**, 1.

shorter and do not enter the water. A second series of horizontal connected pipes—as long as the bath and likewise two inches apart—is suspended close to the top of the air space. The section of vertical pipes in front of the window is removable, being connected, by means of flexible hose couplings, on the one hand to the remainder of the vertical system, and on the other to the horizontal system above. It can also be moved from side to side in the vertical plane, whenever a pipe obstructs the view of a manometer, by means of cords which run through the end walls of the bath. The water passes continuously, first through the system of vertical pipes, and then through that of the horizontal ones in the upper part of the air space. The superficial area of the portion of the pipes lying wholly within the air space is equal to that of all the walls of the air space, including that of the top, and the ratio of the submerged to the unsubmerged portion of pipes is about 1 to 2. The water employed in regulating the temperature of the bath is brought directly from the basement in a large pipe with no intervening outlets. The arrangements by means of which the water in the bath is kept in constant motion, and by which the air above is made to pass continuously through pipes lying in the water have been described in a former paper.[1] The temperature of the bath cannot be so exactly regulated by the means described above as by the automatic devices described in an earlier paper;[2] but the latter are serviceable, of course, only when a temperature somewhat above that of the surrounding air is to be maintained. The essential conditions are that the fluctuations of temperature in the bath shall not be rapid enough during any one experiment to produce "*thermometer effects*"[3] in the cells and that any given series of measurements shall be carried through at approximately the same temperature. During seasons of moderately uniform mean daily temperatures, as in winter, a judicious regulation of the flow of the water through the pipes suffices, but during seasons of continuously and rapidly rising or falling mean temperatures, as in portions of spring and autumn, a further expedient is necessary, both to

[1] This Journal, **36**, 1.
[2] *Ibid.*, **36**, 1.
[3] *Ibid.*, **34**, 23 and 92; **36**, 1.

avoid *thermometer effects* and to secure a period of generally uniform temperatures sufficiently prolonged to enable us to complete a series of measurements. At such times boxes of ice are placed in the bath, both in the water and in the air space above. In this way, by carefully regulating the quantities of the melting ice and the rate of flow of the water, it is possible to secure moderately uniform temperature conditions for a long time, despite unfavorable weather conditions.

The present series of measurements was made during February, March and April. The highest temperature of the water in the bath during that time was 6°.05, and the lowest was 4°.33. The mean bath temperatures and the extreme changes of temperature while the cells were in the bath are given for each experiment in the following table:

Table I.

Mean bath temperatures.	Extreme variation.	Mean bath temperatures.	Extreme variation.
4°.84	0°.8	5°.03	0°.5
4°.93	0°.8	6°.05	0°.7
4°.58	0°.6	4°.35	0°.3
6°.05	0°.7	4°.55	0°.35
4°.50	0°.15	4°.48	0°.75
4°.50	0°.15	4°.33	0°.15
4°.48	0°.9	4°.33	0°.10
4°.51	0°.7	5°.23	0°.5
4°.34	0°.5	4°.60	0°.7
5°.23	0°.5	4°.32	0°.35

The sugar which was used in this series of measurements was from the same supply as that which was employed in an earlier one, and the tests which were applied, in order to ascertain the degree of its purity, have already been described.[1]

Tables II. to XXI., inclusive, give all necessary data relating to the individual experiments. In these the results are corrected for loss in rotation in two of the three possible ways which have been discussed in a former paper,[2] *i. e.*, as they would stand: (1) if all loss in rotation is ascribed to inversion, and no account is taken of dilution; (2) if one-half the total loss in rotation is

[1] THIS JOURNAL, **37**, 426.
[2] *Ibid.*, **37**, 427.

ascribed to dilution and inversion is ignored. We have already given our reasons for believing that the true osmotic pressures of our cane-sugar solutions lie somewhere between these two sets of values, and probably nearer to the latter than to the former.

In Table XXII. are given for each experiment: 1, the upward displacement of the manometer; 2, the loss in rotation in degrees and in percentage of original rotation; 3, the fraction of an atmosphere which is deducted as a correction from the observed pressure when all loss in rotation is ascribed to dilution; 4, the correction which is added to the observed pressure when one-half the loss in rotation is ascribed to dilution and no attempt is made to correct for inversion; and 5, the sum of the two corrections, 3 and 4.

The displacements of the manometers (column 3) were in all cases too slight to affect sensibly the concentration of the solutions. It is clear also that no considerable portion of the dilution of the cell contents was due to distortions of the stoppers since any movement whatever in the material of the stopper is necessarily attended by a displacement of the manometer. Equally satisfactory conditions in respect to the rigidity of the stoppers were secured in the two preceding series of measurements,[1] and it is believed that in the future we have nothing to fear from what was formerly one of the most persistent and troublesome sources of error in measurements of pressure.

The mean loss in rotation of the solutions while in the cells (column 5) was 1.28 per cent while in the Series II.[2] and III.[3] of the measurements with cane-sugar, it was 2.8 and 1.47 per cent respectively. In the case of Series II., there were considerable displacements of the manometer, and no doubt a portion of the relatively large loss in rotation was due to that cause. In Series III. on the other hand, the displacements were insignificant, hence the reduction of the mean loss in rotation, from 1.47 per cent in Series III. to 1.28 per cent (IV.), is to be ascribed to the improvements in method and manipulation which have been introduced in the more recent work. It may not be out

[1] This Journal, **27**, 437.
[2] *Ibid.*, **28**, 39.
[3] *Ibid.*, **27**, 457.

Table II.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 12°.55 at 20° C.
Rotation at conclusion of exp't, 12°.45 at 20° C.
Loss in rotation, 0°.1 = 0.8 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 4.15 P.M., Feb. 14, 1907.

Experiment No. 1.
Manometer used, No. 5.
Capillary depression, 0.02.
Cell used, H.
Resistance of membrane, 219,000.
Initial pressure, 2.15 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 14.											
9.00 P.M.	(5°.4)	6°.95	156.02	152.14	1.00	0.48	0.01	0.02			
Feb. 15.											
10.00 A.M.	4°.95	5°.9	153.20	149.96	1.00	0.48	0.01	0.02	2.39	2.27	0.12
1.00 P.M.	4°.6	6°.0	153.57	150.26	1.00	0.48	0.01	0.02	2.39	2.26	0.13
5.10 P.M.	4°.5	5°.9	153.61	150.36	1.00	0.48	0.01	0.02	2.38	2.26	0.12
Feb. 16.											
10.30 A.M.	5°.3	6°.3	153.49	150.03	1.00	0.48	0.01	0.02	2.39	2.27	0.12
	4°.84		Displacement of manometer = 0.4 mm.						2.39		

Correction, if all loss in rotation is ascribed to inversion = 0.01 atmosphere.
Osmotic pressure = 2.39 atmospheres.
Molecular osmotic pressure = 23.88.
Molecular gas pressure = 22.65.
Ratio of osmotic to gas pressure = 1.053.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.01 atmosphere.
Osmotic pressure = 2.41 atmospheres.
Molecular osmotic pressure = 24.10.
Ratio of osmotic to gas pressure = 1.062.

Table III.

Original wt. normal concentration of solution, 0.1.
Rotation of original solution, 12°.55 at 20° C.
Rotation at conclusion of exp't 12°.45 at 20° C.
Loss in rotation, 0°.1 = 0.8 per cent.
Calibration units of air in manometer, 435.09.
Time of setting up cell, 4.15 P.M., Feb. 14, 1907.

Experiment No. 2.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, I.
Resistance of membrane, 220,400.
Initial pressure, 2.16 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 14.											
9.00 P.M.	(5°.4)	6°.95	160.88	156.88	1.00	0.48	0.01	0.02			
Feb. 15.											
10.00 A.M.	4°.95	5°.9	153.46	150.21	1.00	0.48	0.01	0.02	2.39	2.27	0.12
1.00 P.M.	4°.60	6°.0	153.92	150.61	1.00	0.45	0.01	0.02	2.38	2.26	0.12
5.10 P.M.	4°.50	5°.9	153.51	150.26	1.00	0.48	0.01	0.02	2.39	2.26	0.13
Feb. 16.											
12.10 A.M.	5°.30	6°.6	153.47	149.84	1.00	0.48	0.01	0.02	2.39	2.27	0.12
10.30 P.M.	5°.30	6°.3	153.02	149.56	1.00	0.48	0.01	0.02	2.40	2.27	0.13
	4°.93		Displacement of manometer = 0.34 mm.						2.39		

Correction, if all loss in rotation is ascribed to inversion = 0.01 atmosphere.
Osmotic pressure = 2.39 atmospheres.
Molecular osmotic pressure = 23.90.
Molecular gas pressure = 22.66.
Ratio of osmotic to gas pressure = 1.053

Correction, if one-half the loss in rotation is ascribed to dilution = 0.01 atmosphere.
Osmotic pressure = 2.41 atmospheres.
Molecular osmotic pressure = 24.10.
Ratio of osmotic to gas pressure = 1.062

Table IV.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
Rotation of original solution, 25°.1 at 18° C. Manometer used, No. 5.
Rotation at conclusion of experiment, 24°.8 at 18°C. Capillary depression, 0.02.
Loss in rotation, 0°.3 = 1.20 per cent. Cell used, B.
Calibration units of air in manometer, 434.98. Resistance of membrane, 366,700
Time of setting up cell, 5.30 P.M., Feb. 23, 1907. Initial pressure, 3.38 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 23.											
9.00 P.M.	(5°.1)	(6°.4)	(89.13)	(87.09)	1.02	0.58	0.04	0.02	(4.54)	(4.54)	(0.00)
Feb. 24.											
10.00 A.M.	(4°.8)	(5°.8)	(86.45)	(84.66)	1.02	0.58	0.04	0.02	(4.68)	(4.53)	(0.15)
3.30 P.M.	(4°.5)	(5°.4)	(86.54)	(84.86)	1.01	0.58	0.04	0.02	(4.68)	(4.53)	(0.15)
9.30 P.M.	4°.4	5°.5	86.59	84.88	1.00	0.58	0.04	0.02	4.69	4.53	0.16
Feb. 25.											
9.30 A.M.	5°.0	5°.9	86.36	84.53	1.00	0.58	0.04	0.02	4.71	4.54	0.17
3.00 P.M.	4°.4	5°.7	86.45	84.68	1.00	0.58	0.04	0.02	4.70	4.53	0.17
5.30 P.M.	4°.5	6°.0	86.49	84.62	1.00	0.58	0.04	0.02	4.70	4.53	0.17
	4°.58		Displacement of manometer = 0.22 mm.						4.70		

Correction, if all loss in rotation is ascribed to inversion = 0.04 atmosphere.
Osmotic pressure = 4.70 atmospheres.
Molecular osmotic pressure = 23.50.
Molecular gas pressure = 22.67.
Ratio of osmotic to gas pressure = 1.038.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.03 atmosphere.
Osmotic pressure = 4.77 atmospheres.
Molecular osmotic pressure = 23.85.
Ratio of osmotic to gas pressure = 1.053.

Table V.

Original wt. normal concentration of solution, 0.2. Experiment No. 2.
Rotation of original solution, 24°.8 at 21° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 24°.75 at 21° C. Capillary depression, 0.02.
Loss in rotation, 0°.05 = 0.2 per cent. Cell used, B.
Calibration units of air in manometer, 435.09. Resistance of membrane, 275,000.
Time of setting up cell, 4.45 P.M., March 16, 1907. Initial pressure, 4.03 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 17.											
10.30 A.M.	5°.75	6°.8	86.49	84.38	1.01	0.57	0.01	0.02	4.73	4.55	0.18
3.30 P.M.	5°.8	7°.0	86.47	84.30	1.00	0.57	0.01	0.02	4.74	4.55	0.19
March 18.											
10.00 A.M.	6°.45	7°.55	86.18	83.86	1.01	0.57	0.01	0.02	4.76	4.56	0.20
1.30 P.M.	6°.2	7°.4	86.26	83.98	1.01	0.57	0.01	0.02	4.75	4.56	0.19
	6°.05		Displacement of manometer = 0.04 mm.						4.75		

Correction, if all loss in rotation is ascribed to inversion = 0.01 atmosphere.
Osmotic pressure = 4.75 atmospheres.
Molecular osmotic pressure = 23.73.
Molecular gas pressure = 22.78.
Ratio of osmotic to gas pressure = 1.042.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.00 atmosphere.
Osmotic pressure = 4.76 atmospheres.
Molecular osmotic pressure = 23.80.
Ratio of osmotic to gas pressure = 1.044.

Table VI.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
Rotation of original solution, 36°.6 at 20°.5 C. Manometer used, No. 5.
Rotation at conclusion of exp't, 36°.3 at 20°.5 C. Capillary depression, 0.02.
Loss in rotation, 0°.3 = 0.82 per cent. Cell used, D.
Calibration units of air in manometer, 434.98. Resistance of membrane, 220,000.
Time of setting up cell, 11.45 A.M., April 2, 1907. Initial pressure, 5.98 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
April 2.											
3.00 P.M.	(4°.6)	9°.2	61.11	59.11	1.00	0.61	0.04	0.02			
5.20 P.M.	4°.45	9°.5	60.34	58.31	1.00	0.61	0.04	0.02	7.05	6.79	0.26
8.45 P.M.	4°.45	7°.9	59.94	58.25	1.00	0.61	0.04	0.02	7.06	6.79	0.27
April 3.											
9.45 A.M.	(4°.4)	5°.8	59.60	58.36	1.01	0.61	0.04	0.02	(7.03)	6.79	0.24
12.00 M.	4°.5	6°.6	59.66	58.25	1.00	0.61	0.04	0.02	7.06	6.79	0.27
2.30 P.M.	4°.6	7°.4	59.75	58.17	1.00	0.61	0.04	0.02	7.07	6.79	0.28
	4°.5		Displacement of manometer = 0.07 mm.						7.06		

Correction, if all loss in rotation is ascribed to inversion = 0.04 atmosphere.
Osmotic pressure = 7.06 atmospheres.
Molecular osmotic pressure = 23.53.
Molecular gas pressure = 22.63.
Ratio of osmotic to gas pressure = 1.040.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.03 atmosphere.
Osmotic pressure = 7.13 atmospheres.
Molecular osmotic pressure = 23.77.
Ratio of osmotic to gas pressure = 1.050.

Table VII.

Original wt. normal concentration of solution, 0.3. Experiment No. 2.
Rotation of original solution, 36°.6 at 20°.5 C. Manometer used, No. 6.
Rotation at conclusion of exp't., 36°.3 at 20°.5 C. Capillary depression, 0.02.
Loss in rotation, 0°.3 = 0.82 per cent. Cell used, G.
Calibration units of air in manometer, 396.89. Resistance of membrane, 138,000.
Time of setting up cell, 12.00 M., April 2, 1907. Initial pressure, 5.44 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
April 2.											
3.00 P.M.	(4°.6)	9°.2	55.93	54.06	1.00	0.63	0.04	0.02	(6.95)	6.79	
5.20 P.M.	4°.45	9°.5	55.58	53.71	1.00	0.63	0.04	0.02	7.00	6.79	0.21
8.45 P.M.	4°.45	7°.9	55.23	53.68	1.00	0.63	0.04	0.02	7.00	6.79	0.21
April 3.											
9.45 A.M.	(4°.4)	5°.8	54.99	53.84	1.01	0.63	0.04	0.02	(6.97)	6.79	0.18
12.00 M.	4°.5	6°.6	55.04	53.74	1.00	0.63	0.04	0.02	7.00	6.79	0.21
2.30 P.M.	4°.6	7°.4	55.19	53.73	1.00	0.63	0.04	0.02	7.00	6.79	0.21
	4°.5								7.00		

Displacement of manometer = 0.07 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.04 atmosphere.
Osmotic pressure = 7.00 atmospheres.
Molecular osmotic pressure = 23.33.
Molecular gas pressure = 22.63.
Ratio of osmotic to gas pressure = 1.031.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.03 atmosphere.
Osmotic pressure = 7.07 atmospheres.
Molecular osmotic pressure = 23.57.
Ratio of osmotic to gas pressure = 1.041.

Table VIII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 at 19° C.
Rotation at conclusion of exp't, 47°.6 at 19° C.
Loss in rotation, 0°.4 = 0.83 per cent.
Calibration units of air in manometer, 465.94.
Time of setting up cell, 4.45 P.M., Feb. 25, 1907.

Experiment No. 1.
Manometer used, No. 11.
Capillary depression, 0.02.
Cell used, I.
Resistance of membrane, 182,500.
Initial pressure, 8.11 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 25.											
9.00 P.M.	5°.1	6°.5	48.40	47.27	1.01	0.54	0.06	0.02	9.35	9.07	0.28
Feb. 26.											
10.00 A.M.	4°.4	5°.35	47.85	46.93	1.01	0.54	0.06	0.02	9.42	9.05	0.37
1.45 P.M.	4°.2	5°.6	48.07	47.10	1.01	0.54	0.06	0.02	9.38	9.04	0.34
4.15 P.M.	4°.2	5°.95	48.18	47.15	1.00	0.54	0.06	0.02	9.38	9.04	0.34
	4°.48		Displacement of manometer = 0.03 mm.						9.38		

Correction, if all loss in rotation is ascribed to inversion = 0.06 atmosphere.
Osmotic pressure = 9.38 atmospheres.
Molecular osmotic pressure = 23.46.
Molecular gas pressure = 22.63.
Ratio of osmotic to gas pressure = 1.036.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.04 atmosphere.
Osmotic pressure = 9.48 atmospheres.
Molecular osmotic pressure = 23.70.
Ratio of osmotic to gas pressure = 1.048.

Table IX.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 at 20° C.
Rotation at conclusion of exp't, 47°.1 at 20° C.
Loss in rotation, 0°.9 = 1.88 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 5.15 P.M., March 2, 1907.

Experiment No. 2.
Manometer used, No. 5.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 270,000.
Initial pressure, 7.66 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 2.											
9.00 P.M.	5°.0	6°.5	45.53	44.47	0.99	0.63	0.13	0.02	9.31	9.07	0.24
March 3.											
11.30 A.M.	4°.5	5°.7	45.56	44.63	0.99	0.63	0.13	0.02	9.28	9.05	0.23
3.15 P.M.	4°.4	5°.4	45.56	44.67	0.99	0.63	0.13	0.02	9.27	9.05	0.22
7.30 P.M.	4°.3	5°.4	45.54	44.66	1.00	0.63	0.13	0.02	9.26	9.05	0.21
March 4.											
10.00 A.M.	4°.7	5°.7	45.47	44.54	1.00	0.63	0.13	0.02	9.29	9.06	0.23
1.30 P.M.	4°.4	5°.65	45.45	44.53	1.00	0.63	0.13	0.02	9.29	9.05	0.24
4.45 P.M.	4°.3	5°.8	45.49	44.54	1.00	0.63	0.13	0.02	9.29	9.05	0.24
	4°.51		Displacement of manometer = 0.15 mm.						9.28		

Correction, if all loss in rotation is ascribed to inversion = 0.13 atmosphere.
Osmotic pressure = 9.28 atmospheres.
Molecular osmotic pressure = 23.21.
Molecular gas pressure = 22.64.
Ratio of osmotic to gas pressure = 1.025.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.09 atmosphere.
Osmotic pressure = 9.50 atmospheres.
Molecular osmotic pressure = 23.75.
Ratio of osmotic to gas pressure = 1.050.

Table X.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
Rotation of original solution, 58°.85 at 21° C. Manometer used, No. 5.
Rotation at conclusion of exp't, 58°.15, at 21° C. Capillary depression, 0.02.
Loss in rotation, 0°.75 = 1.27 per cent. Cell used, B.
Calibration units of air in manometer, 434.98. Resistance of membrane, 160,000.
Time of setting up cell, 4.30 P.M., March 5, 1907. Initial pressure, 10.29 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 5.											
9.00 P.M.	4°.7	6°.2	36.61	35.80	0.99	0.64	0.06	0.02	11.76	11.33	0.43
March 6.											
10.00 A.M.	4°.25	5°.3	36.61	35.91	1.00	0.64	0.06	0.02	11.71	11.31	0.40
12.15 P.M.	4°.2	5°.6	36.61	35.87	1.01	0.64	0.06	0.02	11.72	11.30	0.42
3.00 P.M.	4°.2	5°.55	36.58	35.85	1.01	0.64	0.06	0.02	11.72	11.30	0.42
	4°.34		Displacement of manometer = 0.30 mm.						11.73		

Correction, if all loss in rotation is ascribed to inversion = 0.06 atmosphere.
Osmotic pressure = 11.73 atmospheres.
Molecular osmotic pressure = 23.46.
Molecular gas pressure = 22.62.
Ratio of osmotic to gas pressure = 1.037.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.08 atmosphere.
Osmotic pressure = 11.87 atmospheres.
Molecular osmotic pressure = 23.74.
Ratio of osmotic to gas pressure = 1.050.

Table XI.

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
Rotation of original solution, 58°.7 at 21° C. Manometer used, No. 5.
Rotation at conclusion of exp't, 57°.95 at 21° C. Capillary depression, 0.02.
Loss in rotation, 0°.75 = 1.28 per cent. Cell used, B
Calibration units of air in manometer, 434.98. Resistance of membrane, 356,700.
Time of setting up cell, 3.45 P.M., March 14, 1907. Initial pressure, 9.77 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
March 14.											
8.15 P.M.	(5°.4)	6°.95	37.09	36.17	1.00	0.64	0.11	0.02			
March 15.											
10.00 A.M.	5°.5	7°.0	36.53	35.62	1.01	0.64	0.11	0.02	11.75	11.36	0.39
11.00 A.M.	5°.4	6°.4	36.53	35.69	1.01	0.64	0.11	0.02	11.73	11.36	0.37
2.15 P.M.	5°.0	6°.4	36.50	35.66	1.01	0.64	0.11	0.02	11.74	11.34	0.40
3.45 P.M.	5°.0	6°.5	36.50	35.70	1.01	0.64	0.11	0.02	11.72	11.34	0.38
	5°.23		Displacement of manometer = 0.17 mm.						11.74		

Correction, if all loss in rotation is ascribed to inversion = 0.11 atmosphere.
Osmotic pressure = 11.74 atmospheres.
Molecular osmotic pressure = 23.47
Molecular gas pressure = 22.70.
Ratio of osmotic to gas pressure = 1.034.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.08 atmosphere.
Osmotic pressure = 11.93 atmospheres.
Molecular osmotic pressure = 23.86.
Ratio of osmotic to gas pressure = 1.051.

Table XII.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
Rotation of original solution 69°.55 at 19° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 68°.5 at 19° C. Capillary depression, 0.02.
Loss in rotation, 0.05 = 1.51 per cent. Cell used, I.
Calibration units of air in manometer, 435.09. Resistance of membrane, 156,900.
Time of setting up cell, 4.00 P.M., Feb. 21, 1907. Initial pressure, 12.55 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 21.											
9.00 P.M.	(5°.1)	6°.8	30.47	29.73	1.00	0.64	0.17	0.02			
Feb. 22.											
9.45 A.M.	4°.7	6°.5	30.17	29.47	1.01	0.64	0.17	0.02	14.26	13.59	0.67
3.00 P.M.	5°.2	6°.7	30.22	29.49	1.01	0.64	0.17	0.02	14.23	13.61	0.62
4.00 P.M.	5°.2	6°.7	30.25	29.52	1.01	0.64	0.17	0.02	14.22	13.61	0.61
	5°.03		Displacement of manometer = 0.26 mm.						14.24		

Correction, if all loss in rotation is ascribed to inversion = 0.17 atmosphere.
Osmotic pressure = 14.24 atmospheres.
Molecular osmotic pressure = 23.73.
Molecular gas pressure = 22.68.
Ratio of osmotic to gas pressure = 1.047.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.11 atmosphere.
Osmotic pressure = 14.52 atmospheres.
Molecular osmotic pressure = 24.20.
Ratio of osmotic to gas pressure = 1.068.

Table XIII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
Rotation of original solution, 69°.25 at 19° C. Manometer used, No. 11.
Rotation at conclusion of exp't, 68°.55 at 19° C. Capillary depression, 0.02.
Loss in rotation, 0°.7 = 1.01 per cent. Cell used, I.
Calibration units of air in manometer, 465.94. Resistance of membrane, 185,500.
Time of setting up cell, 5.00 P.M., March 16, 1907. Initial pressure, 11.80 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 17.											
10.30 A.M.	5°.75	6°.8	32.13	31.35	1.01	0.56	0.10	0.02	14.33	13.64	0.69
3.30 P.M.	5°.8	7°.0	32.16	31.35	1.00	0.56	0.10	0.02	14.34	13.64	0.70
March 18.											
10.00 A.M.	6°.45	7°.55	32.12	31.25	1.01	0.56	0.10	0.02	14.38	13.68	0.70
1.30 P.M.	6°.2	7°.4	32.14	31.29	1.01	0.56	0.10	0.02	14.36	13.66	0.70
	6°.05		Displacement of manometer = 0.05 mm.						14.35		

Correction, if all loss in rotation is ascribed to inversion = 0.10 atmosphere.
Osmotic pressure = 14.35 atmospheres.
Molecular osmotic pressure = 23.92.
Molecular gas pressure = 22.76.
Ratio of osmotic to gas pressure = 1.051.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.07 atmosphere.
Osmotic pressure = 14.52 atmospheres.
Molecular osmotic pressure = 24.20.
Ratio of osmotic to gas pressure = 1.063

Table XIV.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
Rotation of original solution, 79°.3 at 19° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 78°.3 at 19° C. Capillary depression, 0.02.
Loss in rotation, 1°.0 = 1.26 per cent. Cell used, I.
Calibration units of air in manometer, 435.09. Resistance of membrane, 184,000.
Time of setting up cell, 5.00 P.M., Feb. 16, 1907. Initial pressure, 14.60 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated
Feb. 16.											
9.00 P.M.	(5°.55)	7°.1	26.30	25.63	1.00	0.64	0.15	0.02			
Feb. 17.											
10.30 A.M.	(5°.05)	6°.05	26.29	25.72	1.00	0.64	0.15	0.02			
3.15 P.M.	(4°.85)	6°.0	26.18	25.62	1.00	0.64	0.15	0.02			
Feb. 18.											
11.00 A.M.	4°.5	5°.13	25.95	25.47	1.00	0.64	0.15	0.02	16.59	15.84	0.75
3.35 P.M.	4°.2	5°.28	25.99	25.50	1.00	0.64	0.15	0.02	16.57	15.83	0.74
	4°.35		Displacement of manometer = 0.23 mm.						16.58		

Correction, if all loss in rotation is ascribed to inversion = 0.15 atmosphere.
Osmotic pressure = 16.58 atmospheres.
Molecular osmotic pressure = 23.69.
Molecular gas pressure = 22.62.
Ratio of osmotic to gas pressure = 1.047.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.11 atmosphere.
Osmotic pressure = 16.84 atmospheres.
Molecular osmotic pressure = 24.06.
Ratio of osmotic to gas pressure = 1.063.

Table XV.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
Rotation of original solution, 79°.4 at 21° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 78°.0 at 21° C. Capillary depression, 0.02.
Loss in rotation, 1°.4 = 1.76 per cent. Cell used, B.
Calibration units of air in manometer, 435.09. Resistance of membrane, 260,000.
Time of setting up cell, 6.00 P.M., March 9, 1907. Initial pressure, 13.97 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure-cor rected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 10.											
12.00 M.	(4°.65)	5°.7	25.97	25.44	1.00	0.65	0.21	0.02			
4.00 P.M.	(4°.55)	5°.45	25.99	26.07	1.00	0.65	0.21	0.02			
March 11.											
10.00 A.M.	4°.75	5°.9	25.83	25.28	1.01	0.65	0.21	0.02	16.66	15.86	0.80
12.00 M.	4°.5	5°.6	25.82	25.30	1.01	0.65	0.21	0.02	16.65	15.84	0.81
3.00 P.M.	4°.4	5°.8	25.89	25.35	1.01	0.65	0.21	0.02	16.61	15.84	0.77
	4°.55		Displacement of manometer = 0.49 mm.						16.64		

Correction, if all loss in rotation is ascribed to inversion = 0.21 atmosphere.
Osmotic pressure = 16.64 atmospheres.
Molecular osmotic pressure = 23.77.
Molecular gas pressure = 22.64.
Ratio of osmotic to gas pressure = 1.050.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.15 atmosphere.
Osmotic pressure = 17.00 atmospheres.
Molecular osmotic pressure = 24.29.
Ratio of osmotic to gas pressure = 1.073.

Table XVI.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
Rotation of original solution, 89°.1 at 19° C. Manometer used, No. 5.
Rotation at conclusion of exp't, 87°.55 at 19° C. Capillary depression, 0.02.
Loss in rotation, 1°.55 = 1.74 per cent. Cell used, I.
Calibration units of air in manometer, 434.98. Resistance of membrane, 157,400.
Time of setting up cell, 4.00 P.M., Feb. 27, 1907. Initial pressure, 15.80 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 27.											
9.00 P.M.	4°.9	6°.3	22.62	22.11	1.01	0.66	0.24	0.02	19.10	18.13	0.97
Feb. 28.											
10.30 A.M.	4°.6	5°.55	22.66	22.21	1.01	0.66	0.24	0.02	19.02	18.11	0.91
12.30 P.M.	4°.25	5°.3	22.65	22.22	1.01	0.66	0.24	0.02	19.01	18.09	0.92
4.00 P.M.	4°.15	5°.5	22.71	22.26	1.01	0.66	0.24	0.02	18.97	18.08	0.89
	4°.48		Displacement of manometer = 0.32 mm.						19.03		

Correction, if all loss in rotation is ascribed to inversion = 0.24 atmosphere.
Osmotic pressure = 19.03 atmospheres.
Molecular osmotic pressure = 23.78.
Molecular gas pressure = 22.63.
Ratio of osmotic to gas pressure = 1.051.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.17 atmosphere.
Osmotic pressure = 19.44 atmospheres.
Molecular osmotic pressure = 24.30.
Ratio of osmotic to gas pressure = 1.074.

Table XVII.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
Rotation of original solution, 89°.1 at 21° C. Manometer used, No. 11.
Rotation at conclusion of exp't, 87°.7 at 21° C. Capillary depression, 0.02.
Loss in rotation, 1°.4 = 1.57 per cent. Cell used, I.
Calibration units of air in manometer, 465.94. Resistance of membrane, 87,000.
Time of setting up cell, 4.15 P.M., March 1, 1907. Initial pressure, 17.23 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 1.											
9.45 P.M	4°.4	5°.8	24.06	23.56	1.00	0.57	0.17	0.02	19.20	18.10	1.10
March 2.											
9.00 A.M.	4°.25	5°.5	24.08	23.60	0.99	0.57	0.17	0.02	19.17	18.09	1.08
12.15 P.M.	4°.3	5°.6	24.11	23.62	0.99	0.57	0.17	0.02	19.15	18.09	1.06
3.00 P.M.	4°.3	5°.8	24.14	23.64	0.99	0.57	0.17	0.02	19.14	18.09	1.05
5.15 P.M.	4°.4	6°.05	24.11	23.59	0.99	0.57	0.17	0.02	19.18	18.10	1.08
	4°.33								19.17		

Displacement of manometer = 0.19 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.17 atmosphere.
Osmotic pressure = 19.17 atmospheres.
Molecular osmotic pressure = 23.96.
Molecular gas pressure = 22.62.
Ratio of osmotic to gas pressure = 1.060.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.15 atmosphere.
Osmotic pressure = 19.49 atmospheres.
Molecular osmotic pressure = 24.36.
Ratio of osmotic to gas pressure = 1.077.

Table XVIII.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
Rotation of original solution, 98°.4 at 20° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 96°.8 at 20° C. Capillary depression, 0.02.
Loss in rotation, 1°.6 = 1.63 per cent. Cell used, I.
Calibration units of air in manometer, 435.09. Resistance of membrane, 209,000.
Time of setting up cell, 4.00 P.M., Feb. 19, 1907. Initial pressure

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Feb. 19.											
9.00 P.M.	(4°.5)	5°.8	19.96	19.54	0.99	0.66	0.25	0.02			
Feb. 20.											
10.00 A.M.	4°.4	5°.5	19.82	19.43	0.99	0.66	0.25	0.02	21.84	20.37	1.47
2.45 P.M.	4°.3	5°.5	19.87	19.48	0.99	0.66	0.25	0.02	21.79	20.36	1.43
4.45 P.M.	4°.3	5°.7	19.83	19.42	0.99	0.66	0.25	0.02	21.84	20.36	1.48
	4°.33		Displacement of manometer = 0.19 mm.						21.82		

Correction, if all loss in rotation is ascribed to inversion = 0.25 atmosphere.
Osmotic pressure = 21.82 atmospheres.
Molecular osmotic pressure = 24.25.
Molecular gas pressure = 22.63.
Ratio of osmotic to gas pressure = 1.072.

Correction if one-half the loss in rotation is ascribed to dilution = 0.18 atmosphere.
Osmotic pressure = 22.25 atmospheres.
Molecular osmotic pressure = 24.72.
Ratio of osmotic to gas pressure = 1.093.

Table XIX.

Original wt. normal concentration of solution, 0.9. Experiment No. 2.
Rotation of original solution, 98°.25 at 21° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 96°.6 at 21° C. Capillary depression, 0.02.
Loss in rotation, 1°.65 = 1.68 per cent. Cell used, I.
Calibration units of air in manometer, 435.09. Resistance of membrane, 108,800.
Time of setting up cell, 4.00 P.M., March 14, 1907. Initial pressure, 18.21 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
March 14.											
8.15 P.M.	(5°.4)	6°.95	19.87	19.38	1.00	0.66	0.26	0.02			
March 15.											
10.00 A.M.	5°.5	7°.0	19.74	19.25	1.00	0.66	0.26	0.02	22.02	20.44	1.58
11.00 A.M.	5°.4	6°.4	19.74	19.29	1.00	0.66	0.26	0.02	21.97	20.44	1.53
2.15 P.M.	5°.0	6°.4	19.79	19.34	1.00	0.66	0.26	0.02	21.91	20.40	1.51
3.45 P.M.	5°.0	6°.5	19.78	19.32	1.00	0.66	0.26	0.02	21.93	20.40	1.53
	5°.23		Displacement of manometer = 0.4 mm.						21.96		

Correction, if all loss in rotation is ascribed to inversion = 0.26 atmosphere.
Osmotic pressure = 21.96 atmospheres.
Molecular osmotic pressure = 24.40.
Molecular gas pressure = 22.69.
Ratio of osmotic to gas pressure = 1.075.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.19 atmosphere.
Osmotic pressure = 22.41 atmospheres.
Molecular osmotic pressure = 24.90.
Ratio of osmotic to gas pressure = 1.097.

Table XX.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
Rotation of original solution, 107°.4 at 19° C. Manometer used, No. 11.
Rotation at conclusion of exp't, 105°.7 at 19° C. Capillary depression, 0.02.
Loss in rotation 1°.7 = 1.58 per cent. Cell used, I.
Calibration units of air in manometer, 465.94. Resistance of membrane, 135,000.
Time of setting up cell, 5.00 P.M., March 4, 1907. Initial pressure, 21.39 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.							
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 4.											
10.00 P.M.	5°.0	6°.35	19.13	18.69	1.01	0.58	0.27	0.02	24.24	22.67	1.57
March 5.											
9.00 A.M.	4°.7	5°.75	19.05	18.66	1.00	0.58	0.27	0.02	24.31	22.65	1.66
12.30 P.M.	4°.4	5°.75	19.11	18.72	1.00	0.58	0.27	0.02	24.23	22.63	1.60
3.45 P.M.	4°.3	5°.8	19.13	18.73	1.00	0.58	0.27	0.02	24.21	22.62	1.59
	4°.6		Displacement of manometer = 0.41 mm.						24.25		

Correction, if all loss in rotation is ascribed to inversion = 0.27 atmosphere.
Osmotic pressure = 24.25 atmospheres.
Molecular osmotic pressure = 24.25.
Molecular gas pressure = 22.64.
Ratio of osmotic to gas pressure = 1.071.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.20 atmosphere.
Osmotic pressure = 24.72 atmospheres.
Molecular osmotic pressure = 24.72.
Ratio of osmotic to gas pressure = 1.092.

Table XXI.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.
Rotation of original solution, 107°.5 at 19° C. Manometer used, No. 13.
Rotation at conclusion of exp't, 105°.4 at 19° C. Capillary depression, 0.02.
Loss in rotation, 2°.1 = 1.95 per cent. Cell used, I.
Calibration units of air in manometer, 435.09. Resistance of membrane, 107,500.
Time of setting up cell, 4.30 P.M., March 6, 1907. Initial pressure, 20.94 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
March 6.											
10.00 P.M.	4°.55	5°.95	17.85	17.47	1.01	0.66	0.33	0.02	24.25	22.64	1.61
March 7.											
10.00 A.M.	(4°.2)	5°.3	17.94	17.60	1.01	0.66	0.33	0.02	(24.06)	22.61	1.45
12.15 P.M.	4°.2	5°.4	17.88	17.53	1.01	0.66	0.33	0.02	24.16	22.61	1.55
3.30 P.M.	4°.2	5°.55	17.87	17.51	1.01	0.66	0.33	0.02	24.18	22.61	1.57
	4°.32		Displacement of manometer = 0.59 mm.						24.20		

Correction, if all loss in rotation is ascribed to inversion = 0.33 atmosphere.
Osmotic pressure = 24.20 atmospheres.
Molecular osmotic pressure = 24.20.
Molecular gas pressure = 22.62.
Ratio of osmotic to gas pressure = 1.070.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.24 atmosphere.
Osmotic pressure = 24.77 atmospheres.
Molecular osmotic pressure = 24.77.
Ratio of osmotic to gas pressure = 1.095.

of place to recall here—as having a bearing on the problem of the proper distribution of loss of rotation between inversion and dilution—that in the first series of measurements with glucose,[1] where the displacements of the manometers were considerable, the mean loss in rotation was 1.45 per cent., while in the second series,[2] where there was very little displacement of the manometer, it amounted to 0.90 per cent.

The corrections for inversion (column 6), which are to be *deducted* from the observed pressure if all loss in rotation is ascribed to that cause, range from 0.01 atmosphere for the 0.1 normal solutions to 0.33 atmosphere for one of the normal solutions. The corresponding corrections in the series of measurements with cane sugar in the vicinity of 0° varied from 0.01 to 0.56 atmosphere.

The corrections which are to be *added* to the observed pressures, if one-half the loss in rotation is regarded as dilution and inversion is neglected (column 7), range from 0.00 to 0.24 atmosphere.

Column 8 gives the sums of the corrections presented in columns 6 and 7. They are added because they correct the observed pressures in opposite directions, and are designed to express the limits within which we still question the correctness of our measurements. We have stated elsewhere that we regard the values in column 7 more nearly correct than those in column 6. The reasons for doing so are two in number: first, the inversion as found by the method of Fehling is always much less than that calculated from the whole loss in rotation; second, if half the loss in rotation is, as we believe, due to a dilution of the cell contents which occurs *after* the measurement of pressure, *i. e.*, while the cell is being opened, then the corrections for inversion in column 6 should all be diminished by one-half their value. This point, however, may well remain in abeyance until we have completed the measurements of the osmotic pressure of cane-sugar solutions at other temperatures, and are prepared to subject the whole work to a critical examination, with a view to determining what conclusions may with safety be deduced from the results.

[1] THIS JOURNAL, **37**, 324.
[2] *Ibid.*, **37**, 558.

Table XXII.—Cane-Sugar.

Series IV.

Weight normal concentration.	Number of experiments.	Displacement of manometer. mm.	Loss in rotation.		Corrections.		Limit of uncertainty. Atmosphere.
			1. Degrees.	2. Percentage.	1. If all loss in rotation is ascribed to inversion. Atmosphere.	2. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution. Atmosphere.	
1.	2.	3.	4.	5.	6.	7.	8.
0.1	1	0.40	0°.1	0.80	0.01	0.01	0.02
"	2	0.34	0°.1	0.80	0.01	0.01	0.02
0.2	1	0.22	0°.3	1.20	0.04	0.03	0.07
"	2	0.04	0°.05	0.20	0.01	0.00	0.01
0.3	1	0.07	0°.3	0.82	0.04	0.03	0.07
"	2	0.07	0°.3	0.82	0.04	0.03	0.07
0.4	1	0.03	0°.4	0.83	0.06	0.04	0.10
"	2	0.15	0°.9	1.88	0.13	0.09	0.22
0.5	1	0.30	0°.75	1.27	0.06	0.08	0.14
"	2	0.17	0°.75	1.28	0.11	0.08	0.19
0.6	1	0.26	1°.05	1.51	0.17	0.11	0.28
"	2	0.05	0°.7	1.01	0.10	0.07	0.17
0.7	1	0.23	1°.0	1.26	0.15	0.11	0.26
"	2	0.49	1°.4	1.76	0.21	0.15	0.36
0.8	1	0.32	1°.55	1.74	0.24	0.17	0.41
"	2	0.19	1°.4	1.57	0.17	0.15	0.32
0.9	1	0.19	1°.6	1.63	0.25	0.18	0.43
"	2	0.40	1°.65	1.68	0.26	0.19	0.45
1.0	1	0.41	1°.7	1.58	0.27	0.20	0.47
"	2	0.59	2°.1	1.95	0.33	0.24	0.57

Mean = 1.28 per cent.

Tables XXIII. to XXVIII. inclusive present the results in the various ways which appeared to the authors likely to facilitate examination and comparison.

Table XXIII. gives, for each experiment, (1) the temperature of the solution at which the pressure was measured; (2) the actually observed osmotic pressure, *i. e.*, the pressure *uncorrected for loss in rotation*; (3) the osmotic pressure corrected by ascribing all loss in rotation to *inversion*; (4) the osmotic pressure corrected by ascribing one-half the loss in rotation to *dilution* which precedes the measurement, the other half being supposed to have occurred while the cell was being opened at the close of the experiment and therefore after the measurement; (5) the pressure if a molecular-equivalent quantity of a gas is confined, at the same temperature, to the volume of the solvent in the pure state. In Table XXIV. the same data are presented as mean values for each concentration.

Tables XXV. and XXVI. give the molecular osmotic pressures (*i. e.*, the observed and corrected pressures, each divided by the weight-normal concentration of the solution), also the corresponding molecular gas pressures for the same temperatures.

Finally Tables XXVII. and XXVIII. present the ratios of osmotic to gas pressure, or the values obtained by dividing each of the osmotic pressures—both observed, and corrected for loss in rotation, by the corresponding calculated gas pressure.

Table XXIX. is introduced in order to facilitate a comparison of all the results which have been obtained with cane-sugar. It gives for each concentration of solution (1) the temperature; (2) the osmotic pressure; (3) the molecular osmotic pressure; (4) the calculated molecular gas pressure for the same temperature; and (5) the ratio of observed osmotic to calculated gas pressure. A few explanatory statements will be added for each of the four series.

Series I.—In this series the polariscope was not used. There is, therefore, no means of knowing how far the solutions were diluted from the causes which have been discussed in connection with the later series of measurements. If the loss in rotation was equal to that in Series II.—the first one in which the

Table XXIII.—Cane Sugar.

Series IV.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	Osmotic pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.	Calculated gas pressure at same temperature.
0.1	1	4°.84	2.40	2.39	2.41	2.27
"	2	4°.93	2.40	2.39	2.41	2.27
0.2	1	4°.58	4.74	4.70	4.77	4.53
"	2	6°.05	4.76	4.75	4.76	4.56
0.3	1	4°.50	7.10	7.06	7.13	6.79
"	2	4°.50	7.04	7.00	7.07	6.79
0.4	1	4°.48	9.44	9.38	9.48	9.05
"	2	4°.51	9.41	9.28	9.50	9.05
0.5	1	4°.34	11.79	11.73	11.87	11.31
"	2	5°.23	11.85	11.74	11.93	11.35
0.6	1	5°.03	14.41	14.24	14.52	13.60
"	2	6°.05	14.45	14.35	14.52	13.66
0.7	1	4°.35	16.73	16.58	16.84	15.84
"	2	4°.55	16.85	16.64	17.00	15.85
0.8	1	4°.48	19.27	19.03	19.44	18.10
"	2	4°.33	19.34	19.17	19.49	18.09
0.9	1	4°.33	22.07	21.82	22.25	20.36
"	2	5°.23	22.22	21.96	22.41	20.42
1.0	1	4°.60	24.52	24.25	24.72	22.64
"	2	4°.32	24.53	24.20	24.77	22.62

Table XXIV.—Cane Sugar.

Series IV.

Weight-normal concentration.	Temperature of solution.	Osmotic pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If ½ the loss in rotation is ascribed to dilution.	Calculated gas pressure for same temperature.
0.1	4°.89	2.40	2.39	2.41	2.27
0.2	5°.32	4.75	4.73	4.77	4.55
0.3	4°.50	7.07	7.03	7.10	6.79
0.4	4°.50	9.43	9.33	9.49	9.05
0.5	4°.79	11.82	11.74	11.90	11.33
0.6	5°.54	14.43	14.30	14.52	13.63
0.7	4°.45	16.79	16.61	16.92	15.85
0.8	4°.41	19.31	19.10	19.47	18.10
0.9	4°.78	22.15	21.89	22.33	20.39
1.0	4°.46	24.53	24.23	24.75	22.63

polariscope was used—the pressures should be raised 1.4 per cent on an average—some more than that and some less. The pressures given are those which were actually observed, except a few of the higher ones which have been slightly corrected for a small amount of inversion which was found by the method of Fehling.

Series II.—In this series—as in III. and IV.—the polariscope was used. The mean loss in rotation was 2.8 per cent. The observed pressures have been corrected by ascribing one-half of this loss to dilution which preceded the measurements. They are, therefore, on an average 1.4 per cent higher than the actually observed pressures. The displacements of the manometers were considerable, which renders the corrections for dilution more uncertain than they are thought to be in Series III. and IV. The pressures in this series which are believed to be most in need of revision have been designated by interrogation marks.

Series III.—The displacements of the manometers in this series were negligible. The mean loss in rotation was 1.47 per cent. One-half of this has been ascribed to dilution which occurred while closing the cells. The recorded pressures are therefore, on the average, 0.74 per cent higher than those which were actually observed.

Table XXV.—Cane-Sugar.

Series IV.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	Molecular osmotic pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If ½ the loss in rotation is ascribed to dilution.	Molecular gas pressure.
0.1	1	4°.84	24.00	23.88	24.10	22.65
"	2	4°.93	24.00	23.90	24.10	22.66
0.2	1	4°.58	23.70	23.50	23.85	22.67
"	2	6°.05	23.80	23.73	23.80	22.78
0.3	1	4°.50	23.67	23.53	23.77	22.63
"	2	4°.50	23.47	23.33	23.57	22.63
0.4	1	4°.48	23.60	23.46	23.70	22.63
"	2	4°.51	23.53	23.21	23.75	22.64
0.5	1	4°.34	23.58	23.46	23.74	22.62
"	2	5°.23	23.70	23.47	23.86	22.70
0.6	1	5°.03	24.01	23.73	24.20	22.68
"	2	6°.05	24.08	23.92	24.20	22.76
0.7	1	4°.35	23.90	23.69	24.06	22.62
"	2	4°.55	24.07	23.77	24.29	22.64
0.8	1	4°.48	24.09	23.78	24.30	22.63
"	2	4°.33	24.18	23.96	24.36	22.62
0.9	1	4°.33	24.52	24.25	24.72	22.63
"	2	5°.23	24.69	24.40	24.90	22.69
1.0	1	4°.60	24.52	24.25	24.72	22.64
"	2	4°.32	24.53	24.20	24.77	22.62

Table XXVI.—Cane-Sugar.

Series IV.

Weight-normal concentration.	Temperature of solution.	Molecular osmotic pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If ⅓ the loss in rotation is ascribed to dilution.	Molecular gas pressure.
0.1	4°.89	24.00	23.89	24.10	22.66
0.2	5°.32	23.75	23.62	23.83	22.73
0.3	4°.50	23.57	23.43	23.67	22.63
0.4	4°.50	23.57	23.34	23.73	22.64
0.5	4°.79	23.64	23.47	23.80	22.66
0.6	5°.54	24.05	23.83	24.20	22.72
0.7	4°.45	23.99	23.73	24.18	22.63
0.8	4°.41	24.14	23.87	24.33	22.63
0.9	4°.78	24.61	24.33	24.81	22.66
1.0	4°.46	24.53	24.23	24.75	22.63

Table XXVII.—Cane-Sugar.

Series IV.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	Ratio of osmotic to gas pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If ⅓ the loss in rotation is ascribed to dilution.
0.1	1	4°.84	1.057	1.053	1.062
"	2	4°.93	1.057	1.053	1.062
0.2	1	4°.58	1.046	1.038	1.053
"	2	6°.05	1.044	1.042	1.044
0.3	1	4°.50	1.046	1.040	1.050
"	2	4°.50	1.037	1.031	1.041
0.4	1	4°.48	1.043	1.036	1.048
"	2	4°.51	1.040	1.025	1.050
0.5	1	4°.34	1.042	1.037	1.050
"	2	5°.23	1.044	1.034	1.051
0.6	1	5°.03	1.060	1.047	1.068
"	2	6°.05	1.058	1.051	1.063
0.7	1	4°.35	1.056	1.047	1.063
"	2	4°.55	1.063	1.050	1.073
0.8	1	4°.48	1.065	1.051	1.074
"	2	4°.33	1.069	1.060	1.077
0.9	1	4°.33	1.084	1.072	1.093
"	2	5°.23	1.088	1.075	1.097
1.0	1	4°.60	1.083	1.071	1.092
"	2	4°.32	1.084	1.070	1.095

Series IV.—The displacements of the manometers were wholly negligible as a source of dilution. The mean loss in rotation was 1.28 per cent, one-half of which—as in Series II. and III.—has been corrected for as dilution. Hence the pressures recorded are, on the average, 0.64 per cent higher than those which were observed.

Table XXVIII.—Cane-Sugar.

Series IV.

Weight-normal concentration.	Temperature of solution.	Ratio of osmotic to gas pressure. 1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If ½ the loss in rotation is ascribed to dilution.
0.1	4°.89	1.057	1.053	1.062
0.2	5°.32	1.045	1.040	1.049
0.3	4°.50	1.042	1.036	1.046
0.4	4°.50	1.042	1.031	1.049
0.5	4°.79	1.043	1.036	1.051
0.6	5°.54	1.059	1.049	1.066
0.7	4°.45	1.060	1.049	1.068
0.8	4°.41	1.067	1.056	1.076
0.9	4°.78	1.086	1.074	1.095
1.0	4°.46	1.084	1.071	1.094

In general, the uncertainty regarding the correctness of the pressures recorded in Table XXIX. is believed to be about proportional to the loss in rotation, though absolutely it probably does not exceed one-half of this, *i. e.*, 1.40 per cent for Series II., 0.74 per cent for Series III., and 0.64 per cent for Series IV.

The measurement of the pressures of certain concentrations in the vicinity of 20° will be repeated, especially those of the 0.1, 0.5, 0.6, and 0.7 normal solutions.

There is very little evidence to be discovered in the pressures here given of a temperature coefficient for the osmotic pressure of cane-sugar solutions. The pressures are approximately the same in the vicinity of 0°, 5°, and 20°; and enough has already been learned regarding the pressures at 10° and 15° to lead us to think that these will not differ much from those already found. It is, however, by no means necessary to conclude from the evi-

Table XXIX.—Cane-Sugar.

Weight-normal concentration.		Series I.[1]	Series II.	Series III.	Series IV.
0.1	Temperature	18°.46	24°.14	0°.24	4°.89
	Osmotic pressure	2 .40	2 .60 (?)	2 .44	2 .41
	Molecular osmotic pressure	24 .00	26 .00	24 .40	24 .10
	Molecular gas pressure	24 .00	24 .20	22 .30	22 .66
	Ratio of osmotic to gas pressure	1 .000	1 .074	1 .092	1 .062
0.2	Temperature	20°.75	21°.43	0°.26	5°.32
	Osmotic pressure	4 .74	4 .88	4 .80	4 .77
	Molecular osmotic pressure	23 .70	24 .40	24 .00	23 .83
	Molecular gas pressure	24 .20	24 .00	22 .30	22 .73
	Ratio of osmotic to gas pressure	0 .979	1 .017	1 .075	1 .049
0.3	Temperature	18°.47	20°.73	0°.22	4°.50
	Osmotic pressure	7 .23	7 .36	7 .16	7 .10
	Molecular osmotic pressure	24 .10	24 .53	23 .87	23 .67
	Molecular gas pressure	24 .00	23 .97	22 .30	22 .63
	Ratio of osmotic to gas pressure	1 .000	1 .024	1 .071	1 .046
0.4	Temperature	19°.91	21°.89	0°.24	4°.50
	Osmotic pressure	9 .62	9 .85	9 .40	9 .49
	Molecular osmotic pressure	24 .05	24 .63	23 .50	23 .73
	Molecular gas pressure	24 .13	24 .05	22 .30	22 .64
	Ratio of osmotic to gas pressure	0 .997	1 .024	1 .054	1 .049

[1] The calculations under Series I. were based on H = 1.008, and those under II., III. and IV. on H = 1.000. This will explain certain apparent slight inconsistencies in molecular gas pressures.

Table XXIX. (Continued).

Weight-normal concentration.		Series I.	Series II.	Series III.	Series IV.
0.5	Temperature	20°.58	23°.15	0°.21	4°.79
	Osmotic pressure	12 .09	12 .50 (?)	11 .85	11 .90
	Molecular osmotic pressure	24 .18	25 .00	23 .70	23 .80
	Molecular gas pressure	24 .18	24 .16	22 .28	22 .66
	Ratio of osmotic to gas pressure	1 .000	1 .035	1 .064	1 .051
0.6	Temperature	22°.94	24°.23	0°.22	5°.54
	Osmotic pressure	14 .41	15 .21 (?)	14 .25	14 .52
	Molecular osmotic pressure	24 .02	25 .35	23 .75	24 .20
	Molecular gas pressure	24 .38	24 .25	22 .28	22 .72
	Ratio of osmotic to gas pressure	0 .985	1 .045	1 .066	1 .066
0.7	Temperature	22°.38	23°.85	0°.21	4°.45
	Osmotic pressure	16 .91	17 .63 (?)	16 .81	16 .92
	Molecular osmotic pressure	24 .16	25 .19	24 .01	24 .18
	Molecular gas pressure	24 .33	24 .19	22 .29	22 .63
	Ratio of osmotic to gas pressure	0 .993	1 .041	1 .078	1 .068
0.8	Temperature	18°.73	23°.64	0°.22	4°.41
	Osmotic pressure	19 .43	20 .09	19 .33	19 .47
	Molecular osmotic pressure	24 .29	25 .11	24 .16	24 .33
	Molecular gas pressure	24 .05	24 .20	22 .29	22 .63
	Ratio of osmotic to gas pressure	1 .010	1 .038	1 .085	1 .076

Table XXIX. (Continued).

Weight-normal concentration.		Series I.	Series II.	Series III.	Series IV.
0.9	Temperature	19°.84	24°.78	0°.27	4°.78
	Osmotic pressure	21 .84	22 .58	22 .13	22 .33
	Molecular osmotic pressure	24 .27	25 .09	24 .59	24 .81
	Molecular gas pressure	24 .12	24 .29	22 .29	22 .66
	Ratio of osmotic to gas pressure	1 .006	1 .033	1 .103	1 .095
1.0	Temperature	22°.45	24°.07	0°.25	4°.46
	Osmotic pressure	24 .52	24 .84	24 .78	24 .75
	Molecular osmotic pressure	24 .52	24 .84	24 .78	24 .75
	Molecular gas pressure	24 .34	24 .24	22 .28	22 .63
	Ratio of osmotic to gas pressure	1 .009	1 .025	1 .112	1 .094

dence presented in Table XXIX. and the fact that the pressures at 10° and 15° are about the same as at 0°, 5°, and 20°, that the law of Gay-Lussac does not hold for cane-sugar solutions; for it is still possible that the causes which produce abnormal pressures at 0° disappear gradually, with rising temperature, and at a rate which effectually masks the temperature coefficient of the osmotic pressure. In view of the clear connection which has been established between the deviation at 0° of osmotic from gas pressure, and the deviation of freezing point depression from the calculated value 1.85, it is important to measure, as soon as practicable, the pressures of solutions which exhibit normal freezing point depressions. It is to be anticipated that with such solutions some more definite evidence may be obtained regarding the temperature coefficient of osmotic pressure.

We have learned since the foregoing was written that Professor W. D. Bancroft has felt himself called upon to explain[1] to our colleagues that "Quite recently Morse and Frazer have shown that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent. *They consider this a discovery of their own, quite overlooking the fact that they have simply gone back to van't Hoff's original formulation. Having reached their conclusion empirically*(?), *Morse and Frazer have also overlooked*(?) *that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed.*" We have employed the italics in the above quotation to indicate that portion of it which appears to call for attention on our part, and we have introduced the interrogation marks to designate the particular statements which we must declare unconditionally *to be without foundation in fact.*

The only one of the above three statements which contains an element of truth is the first, and even that requires extensive qualification before our position can be understood.

Our transfer from the volume-normal to what we have designated as the "weight-normal" system was in no dense *empirical.* We made no really formal measurements of osmotic pressure

[1] Jour. Phys. Chem., 10, 320.

with volume-normal solutions except in one instance,[1] when, instead of duplicating the measurement of the 0.9 weight-normal solution with that of another of equal concentration, we measured the pressure of an 0.89101 weight-normal solution, which in concentration is the equivalent of a 0.75 volume-normal one. In other words, we *began the measurement* of pressure with weight-normal solutions. The statement that we took this step "*empirically*," *i. e.*, without a clearly defined reason for it, seems to us to be, on the face of it, altogether lacking in plausibility. However that may be, if Professor Bancroft had been as genuinely anxious to tell the truth about us as he appears to have been to discredit our intelligence, he would hardly have ventured the statement without some ascertained facts to support it.

We do not flatter ourselves that our colleagues in general have taken any particular interest in our mental processes, or that many of them now care to know just how we came to conclude that the weight-normal system is the correct one for the measurement of osmotic pressure. We have taken for granted from the beginning that the principal matters of concern to others than ourselves were the *results*, and have assumed that those who were interested in these would credit us with the exercise of a fair amount of intelligence in the planning and management of the work, until they found evidence in the results themselves for thinking otherwise. Accordingly we have endeavored to abstain, as far as possible, from publishing anything not strictly pertinent either to the method or to the results; and we should have spared our readers much that has been written in regard to the method, were it not for the fact that the weight to be ascribed to the results can only be estimated by the excellence of the method which is employed to secure them.

We should not think it necessary to make explanations for the purpose of correcting Professor Bancroft's impressions regarding our mental capacity, and we should not make them, if that were the only point to be gained. But on two or three occasions we have been surprised by the information—given evidently with the kindly intent of doing us a service, that *there was really an important principle involved in our change of base*

[1] This Journal, **34**, 77.

from the volume-normal to the weight-normal standard. It is this experience, which causes us to think that a brief account of what we have done and why we did it may not be altogether superfluous.

While engaged in an endeavor to develop osmotic cells to a condition in which they would give uniform results, we employed the more conveniently prepared volume-normal solutions, and we were, of course, during that time much more concerned with the difficulties of cell construction than with any of the theoretical aspects of osmotic pressure. However, before the cells had reached a state in which we considered them thoroughly reliable, we were getting, as had been expected, pressures which, according to the then generally prevailing views, were *abnormally high.* This situation was taken seriously into account as soon as the exigencies of the work required it, that is, as soon as the cells were ready for formal measurements of pressure; and with the result that we abandoned the volume-normal and adopted the weight-normal system for the solutions. *The change was made in pursuance of the well defined purpose of ascertaining whether we might not by it effect an automatic correction for the volume of the substance,* and thereby greatly simplify the work which had been undertaken. In other words, we began by attempting to harmonize our practice with what we understood to be the principle of van der Waals as applied to solutions. The result was stated in the following words:[1]

"Soon after beginning the measurement of the osmotic pressure of cane-sugar, under conditions which gave to the results a considerable degree of precision, it became apparent that the *mass of the solvent* plays a part which appears to have been unsuspected hitherto. We found—or *appeared* to discover—that a gram-molecular weight of the substance, dissolved in water and diluted to a liter volume, is not the normal standard for osmotic pressure. On the other hand, *when we dissolved a gram-molecular weight of cane-sugar (342.22 grams) in 1,000 grams of water, i. e., in that mass of the solvent which has the unit volume, 1 liter at the temperature of maximum density—we found its osmotic pressure, at about 20°, in quite close accord*

[1] THIS JOURNAL, **34**, 28.

with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i. e., to that volume which the unit mass of the solvent has at the temperature of greatest density."

"The osmotic pressures of solutions ranging in concentration from 0.05 to 1 gram-molecular weight of sugar, in 1,000 grams of water have since been measured and the results are all reasonably in accord with the hypothesis of van't Hoff, that *osmotic pressure obeys the laws of gases*, provided we accept, as the standard for the solvent, the fixed mass of 1,000 grams of water. These results, together with most of the data employed in calculating them, are presented in the latter part of this paper."

The above passage, taken from our first paper on the osmotic pressure of cane-sugar solutions, contains whatever foundation there may be for the statement: "They consider this" (namely, "that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent") "a discovery of their own, quite overlooking the fact that they have simply gone back to van't Hoff's original formulation."

Granting that we did suppose ourselves to have discovered the fact that "the volume," as far as osmotic pressure is concerned, is to be defined as the *volume of the solvent*, and in no case as the *volume of the solution*, because when it is so defined, the pressures of concentrated solutions of cane-sugar conform as well to the rule of van't Hoff as do the dilute ones; the question arises whether there was, under the circumstances, a reasonable ground for so thinking. We did not then know, and we have not since learned that any one had anticipated us with a definite statement of equivalent significance regarding osmotic pressure, and it may be fair to ask Professor Bancroft whether, in presenting the subject of osmotic pressure previous to 1905, he had been accustomed to define the standard for the comparison of osmotic with gas pressure as the *volume of the solvent*.

While we were considering a change from the volume-normal to the weight-normal system of solutions, because the latter appeared to contain within itself the correction for the volume of the dissolved substance, we made some effort to ascertain whether

we had been anticipated in this matter. Both of the principal authors of this paper examined very carefully the famous paper[1] of van't Hoff, and neither of us could discover that the author of it had definitely provided a way for dealing with what afterwards came to be known as the *"abnormally"* high pressures of concentrated solutions. On the contrary, he seemed to us expressly to limit his deductions to dilute solutions. At the conclusion of Section I, entitled "Der Osmotische Druck. Art der Analogie, welche durch dessen Einführung entsteht," he says: (page 483) "Von diesem praktischen Vorteil werden wir im Nachfolgenden Nutzen ziehen, speziell zur Erforschung der für *'ideale Lösungen'* giltigen Gesetze, *für Lösungen also, die derartig verdünnt sind, dass sie den idealen Gasen an die Seite zu stellen sind, und in denen somit die gegenseitige Wirkung der gelösten Moleküle zu vernachlässigen ist, wie auch der von diesen Molekülen eingenommene Raum bei Vergleich mit dem Volum der Lösung selbst.*" The succeeding three sections, namely, II., III. and IV., are entitled:

II. "Boyle's Gesetz *für verdünnte* Lösungen."
III. "Gay-Lussac's Gesetz *für verdünnte* Lösungen."
IV. "Avogadro's Gesetz *für verdünnte* Lösungen."

On page 493 van't Hoff says: "Der direckt ermittelte osmotische Druck einer Zuckerlösung ist also bei derselben Temperatur volkommen der Spannkraft eines Gases gleich, *das ebenso viele Moleküle enthält als Zuckermoleküle im selben Volum der Lösung vorhanden sind.*" Again, on page 498 we find: "Noch trefflicher ist, dass der so allgemein auch für Lösungen angenommene Guldberg und Waagesche Satz thatsächlich als einfache Schlussfolgerung aus den *oben für verdünnte Lösungen aufgestellten Gesetzen* entwickelt werden kann." The italics in the above quotations are ours. The impressions which we received on reading the paper of van't Hoff, when we were confronted by the fact that concentrated *volume-normal* solutions of cane-sugar were giving *"abnormally"* high pressures were: 1st, that van't Hoff had clearly foreseen the difficulties which would arise in connection with the osmotic pressure of concentrated solutions and the causes of them (quotation

[1] Zeitschrift für physikalische Chemie, 1, 479.

from page 483); 2nd, that, on this account, he expressly limited the application of his deductions to dilute solutions, in which these disturbing causes are of little effect; 3rd, that he nowhere in the paper indicates how the foreseen difficulties with concentrated solutions are to be dealt with. The thought which occurred to us while considering the "abnormal" pressures of our concentrated sugar solutions was, in essence: "Why not, for experimental purposes, let these disturbing causes—"gegenseitige Wirkung der gelösten Moleküle.....", wie auch der von diesen Molekülen eingenommene Raum"—correct for themselves, at least approximately, by adopting the weight-normal system of solutions and considering the volume of the *solvent* and not that of the *solution*, as the standard for comparing osmotic with gas pressure?" The fact that the principle of van der Waals was involved in this change of base was not overlooked, for the very essence of the weight-normal system is that it attempts to correct for the volume of the dissolved substance. Both the idea and the practice of applying the correction of van der Walls to concentrated *volume-normal* solutions was at that time quite familiar to chemists, and we ourselves have employed it as one of the tests of the approximate correctness of our measurements, by calculating the *volume-normal* equivalence of our *weight-normal* solutions and then applying the correcting equation.

It seems pertinent to the question under discussion to ask how others interpreted the "*original formulation of van't Hoff*" to which Professor Bancroft says we have unwittingly returned, the real point being, whether van't Hoff had in mind, as the standard for comparing osmotic with gas pressure, *the volume of the solvent*, or *that of the solution*. Under this head we shall quote Ostwald, by introducing a passage from our first paper[1] on the pressure of cane-sugar solutions, and afterwards Nernst, by borrowing a declaration from his Theoretical Chemistry:

In his book on Solutions, Ostwald says: "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*" This statement fairly represents,

[1] THIS JOURNAL, **34**, 93.

we think, the view generally held respecting the proper magnitude of osmotic pressure, and the known deviations from the rule, as given above, have been regarded as abnormalities, to be reconciled in some way, not yet clear, with the supposed law. The results which we have obtained in the measurement of the osmotic pressure of cane-sugar solutions may be summarized in the following words: *Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.* In other words, dissolved cane-sugar exerts an osmotic pressure throughout the *larger volume of the solution, equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent.* Nernst[1] says: "*d. h. der osmotische Druck gelösten Rohrzuckers ist gerade so gross, wie der Gasdruck, den man beobachten würde, wenn man das Lösungsmittel entfernte und die gelöste Substanz den gleichen Raume bei gleicher Temperatur in Gas form erfüllend zurückliesse.*"

Can there be any doubt, in the light of the declarations cited above, which volume—that of the solution or of the solvent—Ostwald and Nernst had in mind as the standard for the comparison of osmotic with gas pressure; or can there be any doubt as to how these authors interpreted the "original formulation of van't Hoff?" And is it a matter for surprise that we also failed to discover in van't Hoff's paper all of that which is now so clear to Professor Bancroft? In this connection it would be interesting to learn just when Professor Bancroft first discovered that these leaders had departed from the true doctrine, as laid down by van't Hoff, and were teaching error; and just when he himself began to teach the original faith.

It is to be remembered that the only direct quantitative measurements of osmotic pressure which were on record when van't Hoff first discussed the application of the gas laws to it were those of Pfeffer, and that these were made with comparatively dilute solutions, in which the difference between the volume of the solution and that of the solvent was of small significance as compared with that of the experimental defects

[1] Theoretische Chemie, 148 (1898).

of the method by which the measurements were made. Van't Hoff clearly designates the causes (see quotation) of *abnormality* of conduct on the part of concentrated solutions, but we cannot see (as does Professor Bancroft) that he tells us how to deal with them, so as to harmonize the pressures of concentrated solutions with those of dilute ones. There is no doubt that van't Hoff would have dealt effectively with the problem if the *experimental* material at hand had made its solution urgent. There was no such material at hand previous to 1905, for it may safely be affirmed that before this time there is not on record a single *direct* measurement of osmotic pressure, except Pfeffer's which, judged by sound standards, deserves to be called *quantitative.* The conviction which developed afterwards that concentrated solutions must exhibit "*abnormal*" pressures was altogether of an inferential character, and due to attempts to estimate the magnitude of the force by so-called "indirect" methods.

In closing this part of our answer to what we think we may justly call Professor Bancroft's allegations respecting our mental capacity and method of work, we wish to say that, to the writer of this paper, the idea of using weight-normal solutions in physical-chemical investigations was not new when the work upon osmotic pressure was begun, that he had, for several years previous to 1905, advocated frequently in laboratory discussions the use of such solutions when practicable, for the reason that *volume-normal* solutions of equi-molecular quantities of different substances are obviously *not truly equivalent,* owing to the varying molecular ratios of dissolved substance to solvent. Though this idea is now more or less familiar to chemists, they appear in their practice not to have generally adopted the obvious remedy for the defects of the *volume-normal* system, *i. e.*, the *weight-normal* system, but they continue, rather, to employ the former and then, in some cases, to apply cumbersome corrections to the results.

The rule is, however, not without exceptions, as is shown in a recent paper[1] by Walden, from which the following is quoted: "Je nachdem wir C auf die Gewichts—oder Volumeneinheit des Lösungsmittels oder der Lösung beziehen, werden wir alsdann

[1] Zeitschrift fur physikalische Chemie, 88, 500.

stark differierende Werte für die Lösungswärme erhalten. Auf meine Anfrage nach der zutreffendsten Bezugseinheit in den vorliegenden Fällen ist mir von van't Hoff folgender Bescheid liebenswürdigst zu teil geworden: "Seit der Arbeit von Morse und Frazer, die nachwiesen, dass der osmotische Druck für Zucker vollständig dem theoretischen Wert entspricht, falls für das Volumen dasjenige des Lösungs-mittels genommen wird, würde ich die C—Werte in der Isochore beziehen auf 1000 ccm. Lösungsmittel." "Infolgedessen ist in den nachstehenden Tabellen die Konzentration C durchweg auf 1000 ccm. des Lözungsmittels bezogen worden." The quotation here introduced may throw some light upon the question as to what van't Hoff himself, at the time of writing his paper, regarded as the standard for the comparison of osmotic with gas pressure—the volume of the solution, or that of the solvent.

Again, R. J. Caldwell in a communication[1] on "The Sucroclastic Action of Acids as Influenced by Salts and Non-Electrolytes," says: "It is now obvious, however, that a fallacy underlay our conclusion in so far as the action of acids is concerned and that a like fallacy more or less affects, if it do not invalidate, the conclusions of previous workers in similar fields. It will be clear that to determine the influence of any added substance this should be made the only variable at first: in point of fact, a second variable—the amount of water present—has also been introduced. Solutions have been prepared, as a rule, by dissolving the various substances to produce a given volume of solution: the result being that water has been displaced in introducing the third substance. Morse and Frazer appear to have been the first to call attention to the consequences of this practice....."

"In all cases, the method of treatment adopted by previous workers has been influenced in the first place, by the prevailing practice of dealing with volume-normal solutions in laboratory work; and subsequently by the conception introduced by van't Hoff that the state of the molecules of a substance in solution may be regarded as analogous to that of the molecules in a gas, *the fact being overlooked that as the concentration is varied the*

[1] Proceedings of the Royal Society, Series A, 78, 272.

proportion of water present is also varied. No attempt has been made to evaluate the chemical influence of the omitted water."

The defect of the volume-normal system is well illustrated by an example which we take from our own records. In a *volume-normal* solution of cane-sugar at 0° the numerical ratio of sugar to water molecules is about 1 : 44.1, while in a *volume-normal* solution of glucose, the ratio at the same temperature is 1 : 49.2. With respect to this ratio then, *i. e.*, that of dissolved substance to solvent, the cane-sugar solution is 11.5 per cent more concentrated than that of glucose, notwithstanding the fact that, in equal volumes, the two solutions contain the same numbers of dissolved molecules. The result of this difference in concentration, stated in terms of osmotic pressure, is about 3.7 *atmospheres*, the pressure of a *volume-normal* solution of glucose at 0° being about 26.2 atmospheres, and that of a *volume-normal* solution of cane-sugar, at the same temperature, about 29.9 atmospheres.[1] Again the changes in concentration of *volume-normal* solutions of the same substance are obviously not at all proportional to the varying quantities of dissolved substance. For example, while the numerical ratio of cane-sugar molecules to those of water in the 1.0 *volume-normal* solution is 1 : 44.1, in the 0.1 *volume-normal* solution it is 1 : 544.1, instead of 441, as it would be if the one solution were in reality 10 times as concentrated as the other.

Professor Bancroft says: "Morse and Frazer have also overlooked that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed." Here again Professor Bancroft has judged our work *exclusively by what he did not know about it.*

Professor Bancroft's assertion to the contrary notwithstanding, we *did not overlook the assumption in question.* The volume relations of solvent, dissolved substance, and solution have been systematically and carefully investigated from the time we began

[1] It will be observed that the proportion 44.1 : 49.2 :: 26.2 : x does not give 29.9 as the value of x, but 29.23. An explanation of this discrepancy would involve a long discussion of certain peculiarities of the volume—states of cane-sugar solutions in the vicinity of 0°, and also of the probable errors of our experimental work. The figures are approximately correct.

to measure osmotic pressure to the present. Before beginning the first series of measurements of the pressure of cane-sugar solutions, *we determined the densities of all the concentrations of solution* which were to be used in that work, and as soon as the measurements were finished, we calculated out the volumes of the solutions and the differences between them and the sums of the separate volumes of solvent and dissolved substance. Again, as a preliminary to the measurement of the pressure of cane-sugar and glucose in the vicinity of 0°, we determined at 0° the densities of all the solutions of both substances whose pressures were to be ascertained, and when the work of measuring had been completed, we calculated out the volume relations mentioned above. Moreover, owing to certain peculiarities of the osmotic pressure in the vicinity of 0° and of the freezing point depressions of cane-sugar solutions, we determined the densities of these, not only at 0°, but also at the temperature of minimum volume, and, as nearly as possible, at the temperature of freezing. Most of the essential data referred to, *i. e.*, the *densities*, had been made public[1] as early as July, 1906, and all of them had been gathered before the close of 1905.

We have acted from the first in accordance with the conviction that we should probably find obscure peculiarities of both osmotic pressure and of freezing point depressions attended by peculiarities in the volume-states of the solutions, and that we might hope to get light on the former by investigating the latter.

We made a discovery quite early in our work, which greatly increased our interest in these very volume relations, which Professor Bancroft assures our colleagues we "have quite overlooked." It was this—that, taking appearances at their face value, the osmotic pressures of cane-sugar and glucose solutions do not obey the law of Gay-Lussac. It is hardly necessary to state that we have not taken appearances at their face value and rejected the law as applied to osmotic pressure. The experience has only served to make us more anxious than before to subject all volume relations of these solutions to a searching investigation, and to convince us of the wisdom of confining our published statements for the present to matters of method, and to the actual

[1] THIS JOURNAL, **34**, 30 and 95; **36**, 91; also Dissertation of B. S. Hopkins, June, 1906.

results and the most obvious conclusions to be drawn from them. A reserve of this kind apparently cannot be understood by Professor Bancroft, and he has accordingly proceeded to give to the chemical public his own interpretation of all those matters concerning our work in respect to which he was entirely ignorant. We, on the other hand, have learned enough about the problem under investigation to convince us that the less we speculate and generalize in public on the uncertain basis of fragmentary results, the less we shall have publicly to recant hereafter. When we have finished our work with a substance, for example cane-sugar, we hope to discuss the whole subject of its osmotic pressure from the standpoint of the larger view which we shall then have of the problem.

For the information of those who have taken a candid interest in the work which Professor Bancroft has misinterpreted so greatly to our discredit, we insert here two tables (A and B) which were calculated as a part of the work on the osmotic pressure of glucose in the vicinity of 0°. They will serve as examples of the tests which we apply to the observed pressures in order to secure what indirect evidence we may as to their approximate reliability. Neither they nor the others like them were intended for present publication, but only for our private information and guidance. We have not reserved evidence of this kind, which we have had at command from the first, because we underestimated its probable value, but because, in our judgment, its full value could not be realized until certain much discussed defects of our method had been overcome. When we can determine osmotic pressure with about the same degree of precision as we can now determine the volumes of the solutions, a large mass of evidence like that in the tables—and already accumulated for past measurements—will be brought out, and its bearing on the problem discussed.

Table A requires but little explanation. Column 2 gives the volume at 0° of the fixed mass of water employed in making the solutions; column 3, the volumes at 0° of the undissolved glucose, the sp. gr. at 0° having been found to be 1.5567; column 4, the sums of the separate volumes of water and glucose; column 5, the volumes at 0° of the solutions; and columns 6

Table A.—Volume Relations of Weight-normal Solutions of Glucose in the Vicinity of 0°.

Weight-normal concentration.	Volume of the water. cc.	Volume of the glucose. cc.	Sum of the volume of water and glucose. cc.	Volume of the solution. cc.	Difference.[1] Cubic centimeters.	Difference.[1] Per cent.
0.1	1000.13	11.48	1011.61	1010.93	0.68	0.07
0.2	"	22.96	1023.09	1021.70	1.39	0.14
0.3	"	34.45	1034.58	1032.55	2.03	0.20
0.4	"	45.93	1046.06	1043.42	2.64	0.25
0.5	"	57.41	1057.54	1054.29	3.25	0.31
0.6	"	68.89	1069.02	1065.22	3.80	0.36
0.7	"	80.37	1080.50	1076.14	4.36	0.40
0.8	"	91.81	1091.99	1087.06	4.93	0.45
0.9	"	103.34	1103.47	1097.94	5.53	0.50
1.0	"	114.82	1114.95	1108.92	6.03	0.54
(1)	(2)	(3)	(4)	(5)	(6)	(7)

[1] These differences, like the osmotic pressure and the depressions of the freezing points of glucose, are proportional to the concentrations of the solutions. The contraction is throughout very nearly equal to $^1/_3$ the volume of 1 molecule of water for each molecule of dissolved glucose.

and 7, the differences—expressed in cubic centimeters and percentage—between the observed volumes of the solutions and the sums of the separate volumes of solvent and dissolved substance. It will be observed that the differences in columns 6 and 7—amounting at most to 0.54 per cent—are probably smaller than are our errors in determining osmotic pressure, and that we should not have gone very far astray if, in the case of glucose, we had "overlooked that" our "method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed." But the statement that we did overlook the assumption in question we have already characterized as "*without foundation in fact.*" The volume relations of cane-sugar solutions—especially of the more concentrated ones—in the vicinity of 0° are not so clear and satisfactory as are those of glucose, hence the determination, already referred to, of their volume-states, not only at 0°, but also at the temperature of minimum volume, and, as far as possible, at that of freezing. From the evidence already in hand, it seems probable that, after we have developed the method of measuring to a state in which it is satisfactory to us, we shall find a clear connection between certain volume-states of cane-sugar solutions and the peculiarities of pressure which they exhibit. Any attempt to discuss this matter would be premature while the pressures observed are possibly erroneous to the extent of a whole percent or more.

Those who have read our papers on the measurement of osmotic pressure have probably observed in them evidences of anxiety regarding "*sources of error*" in the method, and it may be taken for granted that we have been accustomed to gather and to weigh all obtainable indirect evidence bearing on the question of the reliability of the results, *i. e.*, on the question whether the pressures measured were approximately the true osmotic pressures of the solutions. It was to secure evidence of this nature that we determined from the first densities and freezing point depressions, as well as pressures. As intimated above, we regard the public discussion of the evidence gathered as premature, until certain well known sources of error in the method itself have been overcome, and until the work with a

substance is finished; but under the circumstances which called forth what we have here written, a brief statement may not be superfluous of the lines of evidence upon which we have hitherto relied to convince ourselves that we were obtaining nearly correct pressures. They are:

1. The fact that with the same concentration of solution, at a given temperature, we get always the same pressure, irrespective of the cell in which, or the time at which, the measurement is made.

2. The fact that equivalent concentrations of cane-sugar and glucose solutions in the vicinity of 20° give nearly identical pressures, from which the nearly correct molecular weights of the two substances can be calculated.

3. The fact that the pressures of cane-sugar and glucose in the vicinity of 20°, and of glucose in the vicinity of 0°, are quite strictly proportional to the *weight-normal* concentration of the solution.

4. The fact that, while the pressures of both substances in the vicinity of 0° are considerably above the calculated gas pressures, the deviations of the former from the latter are closely parallel to and of nearly equal value with the deviations of the observed depressions of the freezing point from the theoretical value 1.85.

5. The fact that when the estimated pressures of *volume-normal* solutions are corrected in accordance with the principle of van der Waals, the results agree quite closely with the pressures exerted by *weight-normal* solutions.

This is shown by Table B in which column 1 gives the normal concentration, whether *weight* or *volume*; 2, the observed osmotic pressure of *weight-normal* solutions of glucose in the vicinity of 0°; 3, the estimated osmotic pressures of *volume-normal* solutions of glucose at the same temperatures; 4, the pressures in 3 after correction according to van der Waals; 5, the observed molecular pressure of *weight-normal* solutions; 6, the molecular pressure of *volume-normal* solutions, uncorrected; 7, the molecular pressure of *volume-normal* solutions, corrected. The pressures in 3 are calculated with the aid of the ascertained volume of the glucose in the *weight-normal* solutions, and the ob-

Table B.—A Comparison of the Observed Pressures at 0° of Weight-normal Glucose Solutions with Those Obtained by Correcting the Pressures of Volume-normal Solutions by the Equation of van der Waals.[1]

Normal concentration.	Osmotic pressure on weight-normal basis.	Osmotic pressure on volume-normal basis.	Osmotic pressure on volume-normal basis, corrected.	Molecular osmotic pressure on weight-normal basis.	Molecular osmotic pressure on volume-normal basis.	Molecular osmotic pressure on volume-normal basis, corrected.
0.1	2.40	2.42	2.40	23.97	24.23	23.96
0.2	4.65	4.75	4.64	23.24	23.74	23.21
0.3	7.01	7.24	7.00	23.38	24.14	23.33
0.4	9.30	9.70	9.26	23.24	24.25	23.16
0.5	11.65	12.28	11.59	23.29	24.55	23.17
0.6	14.01	14.92	13.91	23.34	24.86	23.18
0.7	16.37	17.61	16.23	23.38	25.16	23.18
0.8	18.77	20.39	18.56	23.45	25.49	23.20
0.9	21.25	23.32	20.96	23.60	25.91	23.29
1.0	23.59	26.16	23.23	23.59	26.16'	23.23
(1).	(2)	(3)	(4)	(5)	(6)	(7)

[1] See A. A. Noyes, Zeit. fur physikalische Chemie, V. 53.

served pressures of the same, and they are, of course, erroneous to the same degree as the experimental work. Nevertheless, if, in employing the *weight-normal* solutions, we are in fact automatically correcting for the *volume of the dissolved substance*, as we suppose, then the values in column 4 should agree with those in 2, and the values in column 7 with those in 5.

In concluding our defence against a criticism, the apparent animus of which cannot be regarded as admirable in any sense, we call attention to the fact that, in the first paper on the osmotic pressure of cane-sugar solutions, we pointed out and emphasized a relation existing between the relative densities and the freezing point depressions of such solutions. This we could do quite consistently with our customary attitude of reserve with respect to publication because the relation in question had been experimentally established by methods of admitted accuracy. The point which we wish to make by recalling the incident is that there was abundant evidence in our earliest published work to convince any fair-minded critic that we were even then neither overlooking nor ignoring the volume relations of the solutions.

JOHNS HOPKINS UNIVERSITY,
May 15, 1907.

THE REACTION OF ORGANIC MAGNESIUM COMPOUNDS WITH CINNAMYLIDENE ESTERS.

I. REACTIONS WITH METHYL CINNAMYLIDENE MALONATE.

By Marie Reimer.

In beginning the study of the action of Grignard's reagent an α-cyancinnamylideneacetic acid it was found that the reaction was much more complex than that of the same reagent with α-cyancinnamic acid.[1] As both of these compounds contain the "crossed" conjugated system $C:CC:O$, it seemed

$$\begin{array}{l} \\ C:N \end{array}$$

probable that in the case of α-cyancinnamylidene acid, the complexity of the reactions was due to the effect of the additional double linkage in the system $C:CC:CC:O$, rather than to the presence of the cyanogen group, although this is known to react with Grignard's reagent.[2] The object of the experiments here described was to begin a study of the influence of this double linkage upon the reactivity of the system $C:CC:O$.

Methyl cinnamylidenemalonate was selected as the first ester of this type to be studied because the results promised to be of interest in connection with the many addition reactions of this substance that have been investigated by others. Thiele and Meisenheimer[3] were the first to study these reactions in connection with Thiele's theory of "partial valences." They found that hydrocyanic acid adds to the ester in the 1,2-position instead of in the 1,4-position as they had anticipated.

$$C_6H_5\overset{4}{C}H:\overset{3}{C}H\overset{2}{C}H:\overset{1}{C}(COOCH_3)_2 + HCN =$$

$$C_6H_5\overset{4}{C}H:\overset{3}{C}H\ \overset{2}{\underset{\displaystyle CN}{C}}H\overset{1}{C}H(COOCH_3)_2.$$

[1] Kohler and Reimer: This Journal, **33**, 333.
[2] Kohler: *Ibid.*, **35**, 386.
[3] Ann. Chem. (Liebig), **306**, 247.

They also found that by reduction with sodium amalgam, 2 hydrogen atoms were taken up by the acid, and concluded that the resulting compound was 1,4-hydrocinnamylidenemalonic acid. This structure was later proved by Riiber[1] who also showed that this compound slowly undergoes rearrangement, the final product being 3,4-hydrocinnamylidenemalonic acid:

$$C_6H_5CH:CHCH:C(COOH)_2 \rightarrow C_6H_5CH_2CH:CHCH(COOH)_2 \rightarrow C_6H_5CH_2CH_2CH:C(COOH)_2.$$

The change of the deep yellow cinnamylidenemalonic acid to a pure white substance under the influence of the sunlight has been proved to be due to the formation of a tetramethylene compound.[2] In this case the addition takes place at the 3,4-double linkage:

$$2C_6H_5CH:CHCH:C(COOH)_2 \rightarrow \begin{matrix} C_6H_5CHCHCH:C(COOH)_2 \\ \quad | \quad | \\ 2(HOOC)C:CHCHC_6H_5. \end{matrix}$$

Kohler[3] found that acid sulphites add to the acid in the 1,2-position to form the compound,

$$C_6H_5CH:CHCH(SO_3K)CH(COOH)_2.$$

When treated with 1 molecule of bromine, methyl cinnamylidenemalonate forms a dibromide in which the 2 bromine atoms are attached to the 3,4-carbon atoms,[4]

$$C_6H_5CHBrCHBrCH:C(COOCH_3)_2.$$

It is known[5] that the reaction of aromatic magnesium halides with α,β-unsaturated esters consists for the most part in 1,4-addition. With aliphatic magnesium compounds, on the other hand, the reaction generally consists in replacement of alkoxyl with alkyl and then addition in the 1,2-position to the

[1] Ber. d. chem. Ges., **37**, 3120.
[2] Riiber: Ber. d. chem. Ges., **38**, 2411.
[3] This Journal, **31**, 243.
[4] Hinrichsen and Triepel: Ann. Chem. (Liebig), **336**, 223.
[5] This Journal, **28**, 21, 153, 333; **36**, 529.

ketone thus formed. The reaction is, however, greatly influenced by the group in the α-position to the carboxyl, "negative" groups diminishing the tendency toward replacement of alkoxyl. In benzalmalonic and α-cyancinnamic esters, for example, where the very negative carboxyl and cyanogen groups are in the α-position, there is no replacement, but addition of both aromatic and aliphatic halides takes place in the 1,4-position.

As a result of the work here described it has been found that with methyl cinnamylidenemalonate the reaction with both aromatic and aliphatic magnesium compounds is 1,4-addition. In the case of the aliphatic compounds the yields of addition product were not quantitative, but never more than a trace of any other substance could be isolated. There is, therefore, no evidence in this case that the additional ethylene linkage in any way affects the result, but as the substance under examination has in the α-position the most negative of all groups, an investigation of other cinnamylidene esters will be necessary before any general conclusions can be reached. Work in this direction is in progress in this laboratory.

EXPERIMENTAL.

The methyl cinnamylidenemalonate used was prepared by the method of Lieberman,[1] as modified by Thiele and Meisenheimer.[2]

Reaction with Phenylmagnesium Bromide.

In the first experiments a solution of the unsaturated ester in absolute ether was added, drop by drop, to an ethereal solution of phenylmagnesium bromide cooled in a freezing mixture. Each drop of the ester produced a yellow precipitate which redissolved at once. When a little less than 1 molecule of the ester to 4 of magnesium compound had been added, the product of the reaction settled as a thick paste and the yellow compound no longer dissolved. When the reaction was carried out in boiling ethereal solution 1 molecule of ester to 2 of magnesium compound could be used. In boiling benzene, the

[1] Ber. d. chem. Ges., **28**, 1439.
[2] Ann. Chem. (Liebig), **306**, 252.

ester and magnesium halide reacted in almost equivalent quantities. In later experiments a large excess of the magnesium compound was used, as it was found in no way to interfere with the result. The ester was added to boiling ethereal solution of phenylmagnesium bromide, the product boiled for a half hour and then decomposed by pouring on crushed ice. Iced hydrochloric acid was added, the solution extracted several times with ether, the ethereal extract washed and dried over calcium chloride.

Methyl β-phenyl-γ-benzalethylmalonate, $C_6H_5CH:CHCH(C_6H_5)CH(COOCH_3)_2$.—This ester crystallized out on evaporation of the ethereal solution prepared as described above. A small quantity of dark colored oil remained after separation of the crystals. By distillation under diminished pressure, this oil was separated into 3 fractions. The first and second were found to be brombenzene and diphenyl, respectively. The third was an almost colorless oil, which, on treatment with concentrated aqueous potassium hydroxide, gave the same acid as that obtained from the ester which crystallized out at first. The yield of ester was excellent: 20 grams from 16 of cinnamylidenemalonate, instead of 21, calculated. It separates from ether in large, rhombic crystals. It is soluble in ether, chloroform, acetone, slightly soluble in ligroin and cold alcohol. It may be purified by crystallization from a small quantity of boiling alcohol, from which it separates in bunches of white prisms. It melts at 94°.

Analysis:

0.1582 gram substance gave 0.4279 gram CO_2 and 0.0886 gram H_2O.

	Calculated for $C_{20}H_{20}O_4$.	Found.
C	74.07	73.76
H	6.17	6.22

The ester is easily hydrolyzed in the cold. Ten grams of ester were dissolved in a considerable quantity of 95 per cent alcohol, and excess of concentrated aqueous potassium hydroxide added. After a few minutes a potassium salt began to separate in very fine, white branching needles. After an hour the liquid

contained a mass of these crystals. The salt was filtered out, washed with alcohol, dissolved in a small quantity of water and absolute alcohol added until crystallization began. After a few minutes a large quantity of fine white needles of the potassium salt had separated. These were filtered, washed with alcohol and repeatedly with ether and dried in a current of air.

Analysis:

I. 0.2081 gram salt gave 0.0921 gram K_2SO_4.
II. 0.2110 gram salt gave 0.0943 gram K_2SO_4.

	Calculated for $C_{18}H_{14}O_4K_2.H_2O$.	Found. I.	II.
K	20.00	19.83	20.02

β-Phenyl-γ-benzal-ethyl malonic acid,

$C_6H_5CH:CHCH(C_6H_5)CH(COOH)_2$.—From the aqueous solution of the pure potassium salt dilute hydrochloric acid precipitates a white, pasty mass, which crystallizes at once. If the acid is prepared from potassium salt which has not been carefully purified it is precipitated as a dark colored oil, which solidifies very slowly in contact with the acid liquid.

The acid is readily soluble in alcohol, ether, and boiling water, very slightly soluble in boiling ligroin and cold water. From hot water it separates in fine white needles. It cannot be purified by crystallization from water as it slowly loses carbon dioxide. The purest specimen was obtained by precipitation from a solution of the carefully purified potassium salt. It was washed repeatedly with water and dried in a current of air. It melts, with decomposition, at 166°.

Analysis:

0.1584 gram substance gave 0.4200 gram CO_2 and 0.0835 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found.
C	72.97	72.31
H	5.40	5.84

The structure of this acid was determined by oxidation. Ten grams of acid were dissolved in dilute sodium carbonate solution and a cold, concentrated solution of potassium permanganate added as long as decolorization took place. After standing 12 hours the excess of permanganate was decomposed by sulphur dioxide, the solution filtered and the filtrate evaporated on the water bath to a volume of 200 cc. Hydrochloric acid precipitated from the cooled solution a large quantity of an acid which, after one crystallization from water, melted sharply at 121°. It was pure benzoic acid. After 24 hours more crystals of benzoic acid had separated. The filtrate was then evaporated to small volume and extracted with ether. On evaporation the ethereal extract deposited a pale yellow solid. This was dried, pulverized and extracted several times with chloroform to rid it of the last traces of benzoic acid. The residue melted, with decomposition, at 170°–171°, the melting-point of phenylcarboxysuccinic acid. The acid was heated to 180° until there was no further evolution of carbon dioxide. The residue, after 1 crystallization from boiling water, melted at 166° to 167°, the melting point of phenylsuccinnic acid. These transformations prove that the original acid is β-phenyl-γ-benzalethylmalonic acid, the oxidation taking place according to the following equation:

$$C_6H_5CH:CHCH(C_6H_5)CH(COOH)_2 + 4O = C_6H_5COOH + C_6H_5CH(COOH)CH(COOH)_2 \rightarrow CO_2 + C_6H_5CH(COOH)CH_2COOH.$$

The reaction of phenylmagnesium bromide with cinnamylidenemalonic ester consists, therefore, in 1,4-addition.

β-Phenyl-γ-benzalbutyric acid,
$C_6H_5CH:CHCH(C_6H_5)CH_2COOH$. — β-Phenyl-γ-benzalethylmalonic acid was heated to 175° until no more carbon dioxide was given off. The yellowish oil, remaining, solidified, on cooling, in bunches of needles. The substance was crystallized from hot 50 per cent alcohol.

The acid is readily soluble in ether, chloroform, boiling alcohol and ligroin. It is slightly soluble in hot water, from which it separates in very long, fine needles. The purest specimen was obtained by crystallization from boiling ligroin. The acid melts at 118°.

Analysis:

0.1846 gram substance gave 0.5467 gram CO_2 and 0.1045 gram H_2O.

	Calculated for $C_{17}H_{16}O_2$.	Found.
C	80.94	80.76
H	6.34	6.28

On oxidizing the acid in the cold a mixture of benzoic and phenylsuccinnic acids was obtained.

Reaction with Methyl Magnesium Iodide.

Methyl β-Methyl-γ-benzalethylmalonate, $C_6H_5CH:CHCH(CH_3)CH(COOCH_3)_2$.— The reaction was carried out in boiling ethereal solution. Each drop of the ester produced a brilliant orange colored precipitate which redissolved at once. After decomposition with ice and hydrochloric acid, the ethereal solution was washed, dried and the ether distilled. A heavy, clear, straw-colored liquid remained. As it did not solidify in a freezing mixture it was distilled under diminished pressure. Almost the whole amount distilled at 210° (30 mm.). The yield of ester was 76 per cent.

Analysis:

0.1749 gram oil gave 0.4418 gram CO_2 and 0.1126 gram H_2O.

	Calculated for $C_{15}H_{18}O_4$.	Found.
C	68.70	68.94
H	6.87	7.14

The ester could easily be hydrolyzed. The oil was dissolved in alcohol, excess of strong aqueous potassium hydroxide added and the mixture allowed to stand about 10 hours. No salt separated from the solution. The alcohol was evaporated off on the water bath, the residue dissolved in water and the solution

extracted with ether. From the aqueous solution hydrochloric acid precipitated an acid as a clear, yellow oil. This was taken up with ether and shaken in a separating funnel with a small quantity of concentrated sodium carbonate solution. The hydrogen sodium salt of the acid separated at once. It was filtered out, washed repeatedly with ether and dried in the air.

The salt separates in white, pearly plates. It is not readily soluble in cold water.

Analysis:

I. 0.1976 gram salt gave 0.0560 gram Na_2SO_4.

II. 0.1619 gram salt gave 0.0463 gram Na_2SO_4.

	Calculated for $C_{13}H_{13}O_4Na$.	Found.	
		I.	II.
Na	9.00	9.18	9.26

β-Methyl-γ-benzalethylmalonic Acid, $C_6H_5CH:CHCH(CH_3)CH(COOH)_2$.—The acid sodium salt was dissolved in water and the acid precipitated. The acid separates as a clear yellow oil which solidifies completely after standing several hours. It is very readily soluble in cold ligroin and only to a very small extent in boiling ligroin. It is very readily soluble in hot water, from which it separates as an oil. It may be purified by suspending it in a large quantity of ligroin and adding just enough ether to give a clear solution. From this mixture it crystallizes in bunches of extremely small, soft white needles. It melts at 120°–121°. It begins to decompose at 130° and loses carbon dioxide rapidly at 150°.

Analysis:

0.1945 gram substance gave 0.4773 gram CO_2 and 0.1155 gram H_2O.

	Calculated for $C_{13}H_{14}O_4$.	Found.
C	66.66	66.91
H	5.98	6.02

As in the case of the phenyl derivative the structure of this acid was determined by oxidation. The acid was dissolved in sodium carbonate solution and potassium permanganate solution added as long as it was decolorized. The excess of permanganate was reduced by sulphur dioxide and the liquid, after

filtration, evaporated to small volume. Dilute hydrochloric acid precipitated benzoic acid, melting at 120°–121°. The filtrate was evaporated to one-half its volume. On cooling, benzoic acid again separated. The filtrate was then evaporated to very small volume and extracted with ether. On evaporation of the ether a heavy straw-colored liquid remained which solidified slowly on standing. It melted, with decomposition at 136°–142°. The melting point of pure methylcarboxylsuccinic acid is 146°. The acid was then heated in a distilling flask to about 200°. Carbon dioxide was given off and a considerable quantity of water distilled over. The bulk of the substance distilled at 230°–240°. This was an oil which solidified in a freezing mixture, but the crystals melted at room temperature, about 30°. The oil was suspended in hot water and a small quantity of potassium carbonate added. A potassium salt crystallized out in long, colorless needles. The salt was dissolved in water, the solution acidified and extracted with ether. On evaporation the ether deposited an acid in white shining plates melting at 111°-112°. This was pyrotartaric acid which melts at 112°, when heated to about 200° gives an anhydride boiling at 247° and melting at 31.5°, and forms a difficultly soluble acid potassium salt. The oxidation of the acid can, therefore, be represented by the following equation:

$$C_6H_5CH:CHCH(CH_3)CH(COOH)_2 + 4O = C_6H_5COOH + CH_3CH(COOH)CH(COOH)_2 \rightarrow CO_2 + H_2O + CH_3CH.CO \diagup O \diagdown CH_2.CO$$

β-Methyl-γ-benzalbutyric acid, $C_6H_5CH:CHCH(CH_3)CH_2COOH$.—This acid was obtained by heating β-methyl-γ-benzalethylmalonic acid to 160° as long as carbon dioxide was given off. A clear, yellow liquid was left which could not be made to solidify in a freezing mixture after several hours. It was dissolved in sodium carbonate, the solution extracted with ether and then acidified. The acid separated as an oil which solidified in contact with the

acid liquid after standing several hours in a freezing mixture. The oil solidified at room temperature after 4 or 5 days.

The acid is readily soluble in all the usual organic solvents. It may be purified by dissolving it in a small quantity of boiling ligroin and cooling the solution suddenly in a freezing mixture. It crystallizes in hard, compact needles melting at 51°–52°.

Analysis:

0.1780 gram substance gave 0.4939 gram CO_2 and 0.1322 gram H_2O.

	Calculated for $C_{12}H_{14}O_3$.	Found.
C	75.78	75.67
H	7.36	7.42

Reaction with Benzalchloride.

The reaction was carried out as in the preceding experiments. As the ethereal solution containing the product of the reaction had a strong odor of dibenzyl it was poured into water and the mixture distilled with steam. A small amount of toluene and a large quantity of dibenzyl distilled over. The oil left suspended in the distilling flask was taken up by ether. As it could not be made to solidify it was hydrolyzed at once and the aqueous solution acidified. An acid separated as an oil which solidified slowly on standing. The substance is readily soluble in ether, alcohol and acetone, very slightly soluble in boiling ligroin and in boiling water from which it crystallizes in fine, white needles. Without purification the acid was heated to 180° as long as carbon dioxide was given off. The oil remaining solidified very slowly. It separated from a large volume of boiling ligroin in clusters of small, straw-colored prisms. As this acid was not pure enough for analysis after 8 recrystallizations from ligroin, it was dissolved in sodium carbonate and oxidized. The oxidation products were benzoic acid and an acid, which, after 3 crystallizations from boiling water, melted sharply at 160°–161°, the melting point of benzylsuccinic acid.

The formation of this acid proves that the reaction involved consists of 1,4-addition, the decomposition of the product having taken place as follows:

$$C_6H_5CH : CHCH(CH_2C_6H_5)CH(COOH)_2 \rightarrow$$
$$C_6H_5CH : CHCH(CH_2C_6H_5)CH_2COOH \rightarrow$$
$$C_6H_5COOH + C_6H_5CH_2CH(COOH)CH_2COOH.$$

CHEMICAL LABORATORY,
Barnard College,
Feb., 1907.

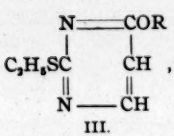
Contributions from the Sheffield Laboratory of Yale University.

CXLV.—RESEARCHES ON PYRIMIDINES: THE ACTION OF METHYL IODIDE ON 2-ANILINO-6-OXYPYRIMIDINE, AND THE SYNTHESIS OF 2-ANILINOPYRIMIDINE.

[TWENTY-FIRST PAPER.]

BY TREAT B. JOHNSON AND F. W. HEYL.

The writers have shown, in a previous paper,[1] that methyl iodide and ethyl iodide react with 2-ethylmercapto-6-oxypyrimidine in presence of alkali, giving 1-methyl-2-ethylmercapto-6-oxypyrimidine, I., and 1-ethyl-2-ethylmercapto-6-oxypyrimidine, II. The formation of isomeric oxygen derivatives, III., or 3-alkyl pyrimidines, IV., was not observed.



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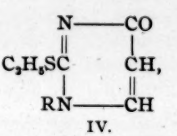

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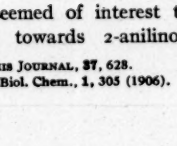

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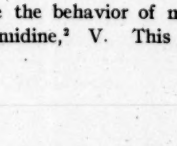


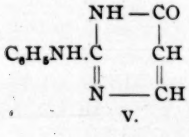
IV.

It seemed of interest to examine the behavior of methyl iodide towards 2-anilino-6-oxypyrimidine,[2] V. This pyr-

[1] THIS JOURNAL, 27, 628.

[2] J. Biol. Chem., 1, 305 (1906).

imidine, theoretically, might give 4 isomeric monomethyl derivatives, *viz.*, 2-anilino-6-methoxypyrimidine, VII., 1-methyl-2-anilino-6-oxypyrimidine, VIII., 2-anilino-3-methyl-6-oxypyrimidine, IX., and 2-methylanilino-6-oxypyrimidine, X.



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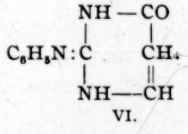

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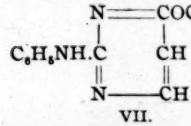

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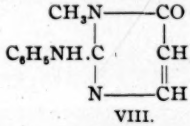

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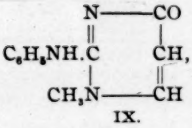

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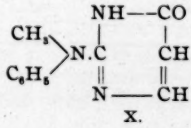
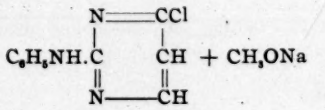
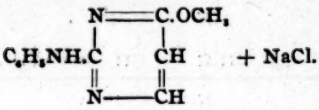


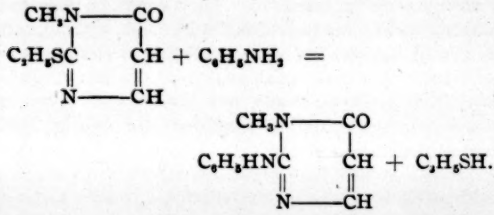
X.

We find that 2-anilino-6-oxypyrimidine, V., reacts with methyl iodide, in the presence of potassium hydroxide, giving two monomethyl derivatives—2-anilino-6-methoxypyrimidine, VII., and 1-methyl-2-anilino-6-oxypyrimidine, VIII. The structure of these two pyrimidines was shown in the following manner: The same methoxypyrimidine (m. p. 119°) was obtained when 2-anilino-6-chlorpyrimidine was warmed with sodium methylate. A quantitative yield of the pyrimidine was also formed when methyl iodide was allowed to act on the silver salt of 2-anilino-6-oxypyrimidine at ordinary temperature.

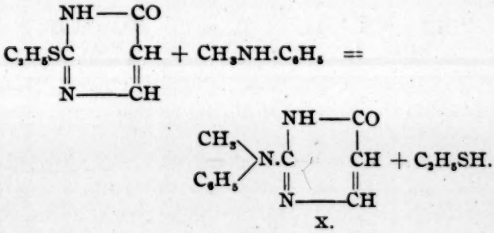




The second isomer was identical with the methyl pyrimidine obtained by heating 1-methyl-2-ethylmercapto-6-oxypyrimidine,[1] I., with aniline at 150°. It was soluble in alkali and

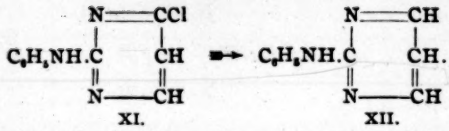


melted at 149°–150°. The isomeric 2-methylanilino-6-oxypyrimidine, X., which was prepared by heating 2-ethylmercapto-6-oxypyrimidine with methyl aniline, melted at 187°.



2-Anilino-6-oxypyrimidine reacts in a smooth manner with phosphorus oxychloride to give 2-anilino-6-chlorpyrimidine, XI. When this was digested with water and zinc dust it was reduced practically quantitatively to 2-anilinopyrimidine, XII.

[1] Johnson and Heyl: *Loc. cit.*



XI. XII.

All attempts to hydrolize 2-anilinopyrimidine, XII., and 2-anilino-6-oxypyrimidine to 2-oxypyrimidine and uracil, respectively, were unsuccessful. They could be digested for hours with concentrated hydrochloric acid without alteration. 2-Anilinopyrimidine was completely decomposed when heated with hydrochloric acid at 168°. On the other hand, 2-anilino-6-oxypyrimidine was not changed by this treatment, and was also recovered unaltered after heating with 20 per cent sulphuric acid at 230°.

The above pyrimidines might be expected to react with carbon bisulphide, giving 2-thiopyrimidine, XIII., and 2-thiouracil, XIV., with formation of phenylisocyanate. We find,

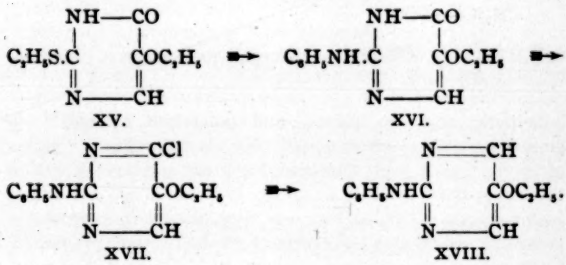
XIII. XIV.

on the other hand, that they are extremely stable in presence of this reagent, and were recovered ualtered after heating with carbon bisulphide at 230°.

We examined, in the course of our work, the action of aniline and ammonia on 2-ethylmercapto-5-ethoxy-6-oxypyrimidine,[1] XV. We find that this mercaptopyrimidine shows no tendency to react with aniline at 100°. In order to introduce the anilino group it was necessary to heat for several hours at 200°. This behavior is of interest since 2-ethylmercapto-6-oxypyrimidine[2] and 2-ethylmercapto-5-brom-6-oxypyrimidine[3] react with aniline at 100° to give quantitative

[1] Johnson and McCollum: J. Biol. Chem., 1, 437.
[2] Johnson and Johns: *Loc. cit.*
[3] Wheeler and Bristol: THIS JOURNAL, 33, 437.

yields of the corresponding 2-anilinopyrimidines. 2-Ethylmercapto-5-ethoxy-6-oxypyrimidine was also recovered unaltered after heating with ammonia at 230°.

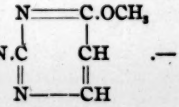


XV. XVI.

XVII. XVIII.

2-Anilino-5-ethoxy-6-oxypyrimidine, XVI., reacted with phosphorus oxychloride to give a good yield of 2-anilino-5-ethoxy-6-chlorpyrimidine, XVII. When this chloride was heated with ammonia a quantitative yield of 2-anilino-5-ethoxy-6-aminopyrimidine was obtained. 2-Anilino-5-ethoxypyrimidine, XVIII., was prepared by reducing the chlorpyrimidine, XVII., with zinc dust.

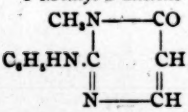
EXPERIMENTAL.

2-Anilino-6-methoxypyrimidine,  .—This pyrimidine was obtained when methyl iodide was allowed to act on the silver salt of 2-anilino-6-oxypyrimidine[1] at ordinary temperature. It was also prepared by treating 2-anilino-6-chlorpyrimidine with sodium methylate. It deposited from 95 per cent alcohol in transparent prisms that melted at 119° to a clear oil. It was converted into 2-anilino-6-oxypyrimidine (m. p. 231°) when digested with 20 per cent hydrochloric acid. Analysis (Kjeldahl):

[1] Johnson and Johns: *Loc. cit.*

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	20.93

1-Methyl-2-anilino-6-oxypyrimidine,



CH_3N——CO / $C_6H_5HN.C$ $CH.H_2O$ / N——CH.—Molecular proportions of 2-anilino-6-oxypyrimidine (20 grams) and potassium hydroxide (6 grams) were dissolved in 95 per cent alcohol. Twenty grams of methyl iodide were then added and the solution heated on the steam-bath until it failed to give an alkaline reaction with turmeric. The solution was then filtered from insoluble potassium iodide and the excess of alcohol evaporated on the steam-bath. We obtained a syrup which deposited a crystalline precipitate when treated with cold water. This was separated and triturated with a 10 per cent sodium hydroxide solution and the insoluble portion purified by crystallization from 95 per cent alcohol. It separated in prismatic crystals that melted at 119° to a clear oil. It was identified as *2-anilino-6-methoxypyrimidine.* A mixture of the 2 compounds melted sharp at 119°. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	21.2

When the sodium hydroxide filtrate (above) was acidified with acetic acid a mixture of 2-anilino-6-oxypyrimidine and 1-methyl-2-anilino-6-oxypyrimidine separated. After a fractional crystallization from alcohol and repeated recrystallizations from benzene and water the methylpyrimidine was obtained pure. It deposited from hot water in slender prisms, that melted at 149°–150° to a clear oil. It contained 1 molecule of water of crystallization, which was determined by heating at 100°–110°.

0.8187 gram substance lost 0.0686 gram.

	Calculated for $C_{11}H_{11}ON_3.H_2O$.	Found.
H_2O	8.21	8.37

Analysis of anhydrous material:

0.2333 gram substance gave 0.5597 gram CO_2 and 0.1130 gram H_2O.

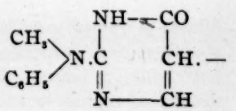
Nitrogen determined by Kjeldahl method:

	Calculated for $C_{11}H_{11}ON_3$.	Found.
C	65.43	65.67
H	5.38	5.47
N	20.89	20.55

Action of Aniline on 1-Methyl-2-ethylmercapto-6-oxypyrimidine.[1]—The mercaptopyrimidine was recovered unaltered after heating with aniline for several hours at 100°. One and two-tenths grams of the mercaptopyrimidine and 0.7 gram of aniline were heated for 7 hours at 125°–155°. The excess of aniline was then removed by distillation with steam and the insoluble residue treated with hot benzene. A crystalline compound separated from the benzene on cooling. It was purified by recrystallization from water and deposited in prisms that melted at 149°–150°. When this derivative was mixed with some *1-methyl-2-anilino-6-oxypyrimidine* (m. p. 149°–150°), the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$.	Found.
N	20.89	20.6

2-Methylanilino-6-oxypyrimidine,

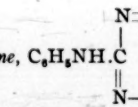


This pyrimidine was prepared by heating 7 grams of 2-ethylmercapto-6-oxypyrimidine[2] with 6 grams of methyl aniline for 14 hours at 100°. It was soluble in warm benzene and alcohol. It separated from hot alcohol in large, prismatic crystals that melted at 187° to a clear oil. The yield corresponded to about 74 per cent of the theoretical. Analysis (Kjeldahl):

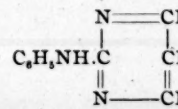
[1] Johnson and Heyl: *Loc. cit.*

[2] Wheeler and Merriam: THIS JOURNAL, **29**, 478 (1903).

	Calculated for $C_{11}H_{11}ON_3$.	Found. I.	II.
N	20.89	20.55	20.66

2-Anilino-6-chlorpyrimidine,  —The hydrochloride of this pyrimidine was obtained when 2-anilino-6-oxypyrimidine was warmed with an excess of phosphorus oxychloride. After the evolution of hydrochloric acid had ceased the solution was poured upon crushed ice to destroy the excess of phosphorus oxychloride. The hydrochloride of 2-anilino-6-chlorpyrimidine separated as a thick varnish, which soon solidified. This salt was triturated with a dilute solution of sodium hydroxide or ammonia when the chlorpyrimidine deposited. It crystallized from alcohol in plates that melted at 134° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{10}H_8N_3Cl$.	Found. I.	II.
N	20.43	20.09	20.3

2-Anilinopyrimidine,  —Five and five-tenths grams of 2-anilino-6-chlorpyrimidine and 30 grams of zinc dust were suspended in 400 cc. of water and the mixture boiled for 2.5 hours. The solution was then filtered and the residue of zinc dust extracted twice with 300 cc. of boiling water. The aqueous filtrates were combined and concentrated to one-half their volume, when the anilinopyrimidine separated, on cooling, in characteristic, slender prisms. The yield was 3.3 grams, or 78 per cent of the theoretical. The base was practically insoluble in cold and difficultly soluble in hot water. It crystallized from 95 per cent alcohol in prismatic crystals that melted at 116° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{10}H_9N_3$.	Found.
N	24.56	24.22

2-Anilinopyrimidine could be boiled with concentrated hydrochloric acid without change. One gram of the base was heated with about 5 cc. of concentrated hydrochloric acid for 2 hours at 148°–168°. Under these conditions it was decomposed into tarry products, from which nothing definite was isolated. An attempt was made to convert 1-anilinopyrimidine into 2-thiopyrimidine by heating with carbon bisulphide. One gram of the pyrimidine was heated with 6 cc. of carbon bisulphide, for 4 hours at 190°–195°. We obtained a clear solution which deposited beautiful, needle-like prisms that melted at 116°. The compound gave no test for sulphur and was identified as unaltered material.

The Hydrochloric Acid Salt.—This salt was extremely soluble in water and alcohol. It had no definite melting point, but decomposed when heated above 125°. Analysis (Kjeldahl):

	Calculated for $C_{10}H_9N_3.HCl$.	Found.
N	20.24	19.77

The Sulphuric Acid Salt.—This salt separated from 20 per cent sulphuric acid in elongated prisms that melted at 140°–142°. The salt dissociates when warmed in aqueous solutions. Analysis:

	Calculated for $C_{10}H_9N_3.H_2SO_4$.	$(C_{10}H_9N_3)_2H_2SO_4$.	Found.
N	15.5	19.09	15.10

The Platinum Chloride Double Salt.—This salt separated in yellow rosettes when a hydrochloric acid solution of the base was treated with hydrogen-platinic chloride. The salt was slowly decomposed in boiling water and metallic platinum deposited. It melted with decomposition at 218°–221°.

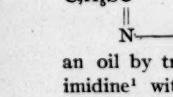
	Calculated for $(C_{10}H_9N_3.HCl)_2.PtCl_4$.	Found.
Pt	25.91	26.6

Behavior of 2-Anilino-6-oxypyrimidine towards Hydrochloric and Sulphuric Acids.—This pyrimidine is more stable in presence of acids than 2-anilinopyrimidine. It was recovered unaltered after heating with concentrated hydrochloric acid for 4 hours at 150°–160°. It was not decomposed after heating with 25 per cent sulphuric acid at 230° for 2 hours.

Behavior of 2-Anilino-6-oxypyrimidine towards Carbon Bisulphide.—There were no indications of any reaction after heating 2 grams of the pyrimidine with 5 cc. of carbon bisulphide for 5 hours, at 150°–160°. The mixture was then heated for 3 hours at 185°–215°. When the tube was opened there was no pressure and the ualtered pyrimidine was recovered melting at 229°. In a third experiment 1 gram of the pyrimidine was heated with 5 cc. of carbon bisulphide for 6 hours, at 230°. When the tube was opened there was some pressure due to the presence of hydrogen sulphide and a crystalline residue was suspended in the carbon bisulphide. This was identified as the unaltered pyrimidine; it melted at 228°–229°, and when mixed with 2-anilino-6-oxypyrimidine the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $C_{10}H_9ON_3$.	Found.
N	22.46	22.17

Hydrochloride of 2-Ethylmercapto-5,6-diethoxypyrimidine,



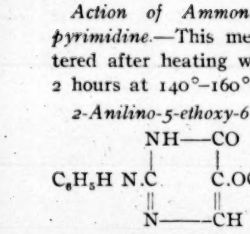
$C_7H_5SC(N{=}C(OC_2H_5)C(OC_2H_5){=}CH{-}N).HCl$.—This pyrimidine was obtained as an oil by treatment of 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine[1] with the calculated quantity of sodium ethylate. When an ether solution of the pyrimidine was saturated with dry hydrochloric acid gas the salt deposited in prismatic crystals that melted with decomposition at 129°–131°. The salt was hydroscopic. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{14}O_2N_2S.HCl$.	Found.
N	10.58	10.55

[1] Johnson and McCollum: J. Biol. Chem., 1, 443 (1906).

Action of Ammonia on 2-Methylmercapto-5-ethoxy-6-oxypyrimidine.—This mercapto pyrimidine was recovered unaltered after heating with concentrated alcoholic ammonia for 2 hours at 140°–160° and again for 1.5 hours at 210°–235°.

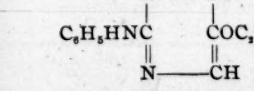
2-Anilino-5-ethoxy-6-oxypyrimidine,



2-Ethylmercapto-5-ethoxy-6-oxypyrimidine[1] was recovered unaltered after heating with aniline on the steam-bath for several hours. Four grams of the mercaptopyrimidine and 2 grams of aniline were dissolved in 10 cc. of alcohol and heated for 2 hours at 185°–216°. When the tube was examined the presence of ethyl mercaptan was apparent, and a crystalline residue had deposited. This was a mixture of unaltered mercaptopyrimidine and the anilino derivative that melted above 160°. The anilino compound was separated from the mercapto derivative by dissolving in cold dilute hydrochloric acid and making alkaline with ammonia. The anilino derivative deposited in plates and was purified for analysis by recrystallization from alcohol. It melted at 231°–232°. In a second experiment we heated 10 grams of the mercaptopyrimidine and 5.1 grams of aniline for 6 hours at 190°–200° and obtained 6.8 grams of crude anilino compound melting at 214°–220°. We did not observe the formation of any 2,5-dianilino-6-oxypyrimidine under the conditions employed. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}O_2N_3$.	Found.
N	18.18	18.10

2-Anilino-5-ethoxy-6-chlorpyrimidine,

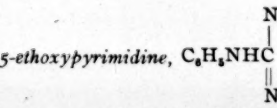


Ten and five-tenths grams of 2-anilino-5-ethoxy-6-oxypyrimidine were warmed with 30 cc. of

[1] Johnson and McCollum: *Loc. cit.*

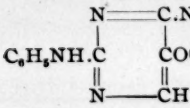
phosphorus oxychloride until the evolution of hydrochloric acid ceased. The solution was then poured upon crushed ice, when the chlorpyrimidine separated as a semi-solid. The chloride was dissolved in ether and thoroughly dried with calcium chloride. When the ether was evaporated the chloride deposited in prismatic crystals that were extremely soluble in organic solvents. The compound crystallized from alcohol in stout prisms, that melted at 111°–112° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}ON_3Cl$.	Found.
N	16.82	16.55

2-Anilino-5-ethoxypyrimidine,  .—One gram of 2-anilino-5-ethoxy-6-chlorpyrimidine was digested for 1 hour with 10 grams of zinc dust and 150 cc. of water. When the hot mixture was filtered the pyrimidine deposited in prismatic crystals. It was difficultly soluble in water and more was obtained by repeatedly extracting the zinc residue with hot water. The pyrimidine dissolves in concentrated sulphuric acid to give a yellow solution. It crystallized from 95 per cent alcohol in short prisms that melted to a clear oil at 130°–131°. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}ON_3$.	Found.	
		I.	II.
N	19.53	18.98	19.33

2-Anilino-5-ethoxy-6-aminopyrimidine,



.—This pyrimidine was obtained when 2-anilino-5-ethoxy-6-chlorpyrimidine was heated with alcoholic ammonia at 180°–188°. When 1 gram of the chloride was heated with alcoholic ammonia, for 2 hours, at 150°,

the reaction was not complete, and the product obtained gave a pronounced test for chlorine after crystallization from alcohol. The pyrimidine crystallized from 95 per cent alcohol in prisms that melted at 133°–134° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{18}H_{14}ON_4$.	Found.
N	24.34	24.06

NEW HAVEN, CONN.,
June 15, 1907.

OBITUARY.

SIR WILLIAM PERKIN.

While the Perkin celebration of last year is still fresh in our memory comes the news of the death of Sir William. His name is so familiar to the world and the main events of his life have so recently been recited that it is not necessary to present here an elaborate notice. He was honored because of the connection between his work on *mauve* and the development of the coal tar color industries.

His first patent, which was in fact the first patent ever granted for the preparation of a coal tar color, was taken out in 1856, and in 1906, the fiftieth anniversary of this event was celebrated.

While Perkin was eminently successful as an industrial chemist, he was also a worker in the field of pure science. "Perkin's reaction" is well known to all who are familiar with organic chemistry. The principal example is the reaction which takes place between benzoic aldehyde, sodium acetate and acetic anhydride, resulting in the formation of cinnamic acid.

Probably his most valuable contribution to chemistry is his masterly investigation "On the Magnetic Rotary Polarisation of Compounds in Relation to Their Chemical Constitution" (1884). He kept up work in this line until his death.

Those who had the pleasure of meeting him on the occasion of his recent visit need not be told that he was a genial, unassuming man.

While fully appreciating all that was being done for him, he did not take the matter too seriously. He was glad when it was all over and he could get back to his beloved home.

He seemed in the best of health and no one could have suspected that it would so soon all be over.

He was born in 1838 and was therefore 69 at the time of his death. I. R.

REVIEWS.

ESSAIS DE JEAN REY, Docteur en Medecin. Edition nouvelle avec Commentaire, publiée par MAURICE PETIT, PHARMACIEN de première classe. Paris: A. Hermann, 1907. 8vo., pp. 190.

About the year 1770 the French Chemist, Bayen, while engaged in investigations on the increase in the weight of metals caused by calcination, discovered a little, old book, published in 1630, entitled "Essays de Jean Rey, sur la Recherche de la Cause pour laquelle l'Estain et le Plomb augmentent de poids quand on les calcine." ..... This volume was republished by Bayen in 1777. Although it is clear that Rey anticipated Lavoisier in showing that the increase in weight caused by calcination is due to something taken up from the air, Rey's name is not often mentioned in connection with this important discovery. In 1896 M. Grimaux caused to be published a new impression of the original text without explanatory notes. Now M. Petit has brought out a new edition with notes and with important letters that passed between Rey and Mersenne. This will be of interest to the student of the history of chemistry. As a translation of Rey's Essay is published as No. 11 of the *Alembic Club Reprints*, it has become well known to English-speaking chemists. Apparently more and more writers in chemistry are coming to recognize the value of Rey's work. The essential feature of his discovery is given in this paragraph.:

"The condensed air attaches itself to the (metallic) calx, and adheres little by little to the smallest of its particles, thus, its weight increases from the beginning to the end. But when all is saturated, it can take up no more. Do not continue your calcination in this hope; you would lose your labour."

Important as Rey's discovery was, it was not sufficient to overthrow the theory of phlogiston. For this purpose work of the kind done by Lavoisier was absolutely necessary. I. R.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER VON DR. CH. M. VON DEVENTER. mit einem vorwort von PROF. DR. J. H. VAN'T HOFF. Dritte auflage vesargt von PROF. DR. ERNST COHEN., Amsterdam: S. L. Van Loog; Leipsig: Wilhelm Englemann. 1906. pp. 161. Price, M. 4.

There is not very much that can be said in connection with this little book. As the title implies, it is an elementary dis-

cussion of the fundamental principles of physical chemistry, presented in a clear and concise form. The book is too elementary and too brief to give more than a very general introduction to the subject, but those who wish only such an introduction will probably find the work helpful. H. C. J.

ELEMENTARY PRACTICAL CHEMISTRY. PART II. Analytical Chemistry, qualitative and quantitative. By FRANK CLOWES, D.Sc., London, Emeritus Professor of Chemistry in University College, Nottingham and J. BERNHARD COLEMAN A.R.C.Sc. Head of the Chemical Department of the Southwestern Polytechnic, Chelsea. Fifth edition. London: J. & A. Churchill, Philadelphia: P. Blakiston's Son & Co., 1907. pp. 237 Price, $1.00 net.

This is a useful volume to those who desire to acquire, in a limited time, some knowledge of qualitative and quantitative analysis. There are 134 pages given to qualitative analysis, 38 pages to volumetric, 24 to gravimetric analysis, and 10 pages to inorganic preparations. E. R.

INORGANIC CHEMISTRY FOR SCHOOLS AND COLLEGES. By JAS. LEWIS HOWE, Washington and Lee University. Being a second edition of Inorganic Chemistry, according to the Periodic Law by F. P. VENABLE and J. L. HOWE. pp. 422. Easton: The Chemical Publishing Co. 1907. Price, $3.00.

The appearance of the first edition of this book was noticed.[1] In the first edition the Periodic System was followed more closely, perhaps, than in any other text-book on general chemistry.

In the present edition this plan is not adhered to so closely, and the result is an improvement in the book. The work begins, like most others, on the same subject, with a study of hydrogen, oxygen and water, the author stating, in his preface, that "It has been found desirable that a student should be well grounded in the general principles of chemistry before entering upon any extended descriptive chemistry. The latter, then, becomes a series of illustrations of the principles, rather than an end in itself."

The author touches, in his preface, upon a fundamental pedagogical principle when he refers to *repetition* as a necessary means in dealing with matters of importance. This is one of the many reasons why the properly conducted "*Quiz*" is of inestimable value in teaching any subject, whether in an elementary manner or from the more advanced standpoint.

The author has introduced a number of up-to-date technical processes, dealing with the applications of chemistry.

H. C. J.

[1] THIS JOURNAL, **30**, 875.

SMALLER CHEMICAL ANALYSIS. By G. L. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science, London. London: Longmans, Green & Co. 1906. pp. 147. Price, 60 cents.

A simple manual of qualitative analysis with a brief chapter on volumetric analysis. The methods employed are the familiar ones, excepting the use of sodium peroxide as the oxidizer in the separation of chromium from aluminium and iron. While the book is good, it requires no special comment.

E. R.

PRACTICAL PHYSICAL CHEMISTRY. By ALEX FINDLAY, M.A., Ph.D., D.Sc., Lecturer on Physical Chemistry, University of Birmingham, with 92 figures in the Text. New York and Bombay: Longmans, Green & Co., London. 1906. pp. 282. Price, $1.20.

The reviewer must take exception to a portion even of the preface of this book. We find that "while, however, the student of practical inorganic or organic chemistry has at his command an abundant supply of text-books, both elementary and advanced, the student of practical physical chemistry has hitherto been forced to rely, almost entirely, on the text-book of Ostwald, or Ostwald and Luther." The author seems to forget that we have a very fair manual, written by Getman, which covers much of the field referred to, and that it is no longer necessary to have our physical chemical guide for the laboratory "made in Germany."

It is rather surprising that the Ostwald method of calibration measuring apparatus should be recommended, when we have so much better methods available.

It is perhaps, even more surprising that the Nernst-Loeb apparatus for determining transference numbers should be given, when we have now at least a dozen superior pieces of apparatus.

Another point where we must criticize the book adversely is in connection with the illustrations. The various pieces of apparatus are very poorly drawn, and poorly reproduced and this detracts greatly from the appearance of the book. Further, the use of the word "molar" for molecular is not to be encouraged in English.

As to the merits of the work, they are not few. The ground covered is adequate for laboratory purposes, and, with the exception of a too great reverence for the antique in the choice of methods and apparatus, is very well covered. The book will, doubtless, prove useful in the laboratory, and it is to be hoped that the minor defects will be removed in the next edition.

H. C. J.